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PROCEEDINGS
# of the
EIGHTH
COTTON UTILIZATION RESEARCH CONFERENCE

Held at New Orleans, Louisiana
May 1 – 3, 1968

Agricultural Research Service
UNITED STATES DEPARTMENT OF AGRICULTURE

PREFACE

The Cotton Utilization Research Conference sponsored annually by the Southern Utilization Research and Development Division brings the results of cotton research (fundamental, chemical modification, and mechanical processing) to the attention of representatives of the textile and allied industries and other interested organizations. This year's program included talks on fundamental studies of the structure and chemistry of cellulose; cotton durable-press products; water and oil repellency; radiation, weather, rot, and flame resistance; and new techniques in mechanical processing.

This Conference was held May 1-3, 1968, at New Orleans, La. The Honorary Chairman was Wilmer Smith, President, Plains Cooperative Oil Mill, and the General Chairman, J. W. Weaver, of Cone Mills Corporation. The program was developed by B. H. Wojcik, Assistant Director, under the general direction of C. H. Fisher, Director, in cooperation with staff members, and advisers representing the cotton industry.

These proceedings report in full or in summary the statements presented by the various speakers during the conference and give an account of the discussions following.

The opinions expressed by the participants appearing at this conference are their own and do not necessarily represent the view of the U.S. Department of Agriculture.

Underscored numbers in parentheses refer to references at the end of each paper. The data presented in the references, figures, and tables are reproduced essentially as they were supplied by the author of each paper.

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WELCOME

by

C. H. Fisher, Director

Southern Utilization Research and Development Division

On behalf of the Southern Utilization Research and Development Division (SURDD), I welcome you to our Eighth Annual Cotton Utilization Research Conference. We are complimented because we have such a splendid audience, both in quality and quantity. We appreciate your interest in cotton research and in our Conferences, and we hope that you will return for other Conferences and visits.

I am pleased because I can welcome you also on behalf of Secretary of Agriculture Orville L. Freeman. I shall read the telegram received yesterday:

> Please welcome on my behalf, all attending our Eighth Cotton Utilization Research Conference. I think of no finer opportunity for our scientists to meet with their colleagues in the industrial and academic communities to report and discuss the latest results of research on cotton. The demand for clothing, household, and industrial textiles continues to grow. Our research responsibility is to develop new and improved cotton products that can compete more effectively for these markets, thereby increasing farm income and providing a better service to consumers. This Conference provides an excellent forum for discussing many aspects of this important work. You have my best wishes for an informative and productive meeting.
>
> Orville L. Freeman, Secretary of Agriculture

I wish to give a special welcome to those present from other countries:

Rafael Audivert, Barcelona, Spain
J. Baines, Sao Paulo, Brazil
Frank Burkitt, Manehester, England
J. H. Bethune, Ontario, Canada
T. Fransen, Ghent, Belgium
Marianne Kärrholm, Gothenburg, Sweden
Martin W. Schwemmer, Zurich, Switzerland
J. O. Warwicker, Manchester, England
G. A. Byrne, Manchester, England

Mr. Byrne is working at SURDD as a fellow supported by the National Cotton Council.

Probably most of you know that the principal purpose of these annual Conferences is to report our cotton research promptly and to receive your comments. We hope you will feel completely free to make comments and suggestions during the Conference and the entire year.

Over the years, we have benefited greatly from the invaluable help and friendly cooperation of many individuals and organizations. I wish to express sincere appreciation to everyone who has provided assistance and encouragement in any form. As one means of expressing our thanks, we have provided a list of our current cotton program advisers. We are highly grateful to both our current and earlier official advisers.

Current Cotton Advisers

John M. Barrell, Mount Vernon Mills, Inc., Baltimore, Md.

George S. Buck, Jr., National Cotton Council of America, Memphis, Tenn.

R. J. Cheatham, Technical Consultant, New Orleans, La.

J. Marshall Cole, Cold Springs Bleachery, Yardley, Pa.

Carl Cox, The Cotton Research Committee of Texas, Dallas, Tex.

J. Lindsay Dexter, P. O. Box 353, Beverly Farms Station, Beverly, Mass.

Brooke Duncan II, The Foster Co., Inc. New Orleans, La.

George R. Eckhardt, Coats & Clark, Inc., Union, N. J.

John P. Elting, Kendall Mills, Charlotte, N. C.

Fred Fortess, Celanese Fibers Marketing Co., New York, N. Y.

P. J. Fynn, J. C. Penney Co., New York, N. Y.

Nelson F. Getchell, National Cotton Council of America, Washington, D. C.

Hermann B. Goldstein, Sun Chemicals Corp., Wood River Junction, R. I.

Otto Goedecke, Otto Goedecke, Inc., Hallettsville, Tex.

L. H. Hance, Fieldcrest Mills, Inc., Eden, N. C.

M. Earl Heard, Research Consultant, Texas Technological College, Lubbock, Tex. (Home: N. 18th Street, West Point, Ga.)

Lawrence L. Heffner, Federal Extension Service, North Carolina State University, Raleigh, N. C.

Donald A. Johnson, Plains Cotton Growers, Inc., Lubbock, Tex.

S. J. Kennedy, U. S. Army Natick Laboratories, Natick, Mass.

J. Edward Lynn, Technical Consultant, Old Greenwich, Conn.

William J. Martin, Federal Extension Service, Clemson University, Clemson, S. C.

Fred Morehead, Technical Consultant, Westchester, Pa.

Maurice Morton, Institute of Polymer Science Research, The University of Akron, Akron, Ohio

Glenn Nesty, Allied Chemical Corp., Morristown, N. J.

James S. Parker, American Textile Manufacturing Company, Charlotte, N. C.

Benjamin Phillips, Union Carbide Corp., New York, N. Y.

Walter C. Regnery, Technical Consultant, Newberry, S. C.

Leonard Smith, National Cotton Council of America, Washington, D. C.

Vernon C. Smith, Collins & Aikman Corp., Albemarle, N. C.

B. S. Sprague, Cellanese Corp. of America, Summit, N. J.

W. A. Turner, Avondale Mills, Sylacauga, Ala.

J. W. Weaver, Cone Mills Corp., Greensboro, N. C.

Leonard Weissbein, American Cyanamid Co., Bound Brook, N. J.

George S. Wham, Good Housekeeping, New York, N. Y.

We are deeply grateful also to those organizations that have supported our cotton research by providing either funds or fellows: Foundation for Cotton Research and Education, Cotton Producers' Institute, National Cottonseed Products Association, International Lead-Zinc Research Institute, National Cotton Council of America, National Batting Institute, Textile Waste Association, Agency for International Development, and U. S. Army Natick Laboratories.

We are indebted to Stephen Kennedy and colleagues at the U. S. Army Natick Laboratories for providing valuable physical facilities and cooperation in the development and evaluation of textile products for defense needs.

It is helpful to have new products of potential utility developed and evaluated in a pilot plant and in an industrial environment. We are able to do this with many new products, processes, and machines because of splendid cooperation of our friends in other organizations. We are naturally very grateful for this invaluable assistance. Examples of cooperation of this kind are:

Bale-Opener-Blender:	Greenwood Mills, Greenwood, S. C.
Insect-Resistant Bag:	Don Walker, Textile Bag Manufacturers' Association; Mr. Laudani and colleagues of Market Quality Research Service, ARS; and Bemis Bag Manufacturing Co.
Improved Sandbag:	King Finishing Company, Dover, Ga.; Stephen Kennedy and colleagues, U. S. Army Natick Laboratories; Mr. Bagdon of Fort Belvoir; Ralph Siu, Army Materials Command.
THPOH: Flame Retardant:	United Merchants and Manufacturers Co., in cooperation with U. S. Army Natick Laboratories; and Reeves Brothers.

Seersucker Suits for Men: National Cotton Council; Gordon Ford Co.

For some time we have been witnessing the construction of a two-story building with approximately 30,000 sq. ft. of floor space. As stated last year, this new building—adjacent to our present building—will house pilot plants for processing cotton. One will process cotton mechanically and the other chemically. This will increase our floor space for cotton research about 30 percent. Completion of the building has been delayed, but we are hopeful now that it will be completed within a few months.

During the past year, our research, conducted in cooperation with many organizations, has continued to be profitable. Some of our research findings have been adopted by other organizations and used for practical purposes, and some of our developments that were commercialized several years ago are being used more extensively.

The national campaign for fire safety and the passage of the new Flammability Act have thrown the spotlight on SURDD research in this area. Some of the flame-retardant treatments used most extensively for fabrics are based upon products of SURDD research, particularly THPC and APO-THPC.

During the year, we announced two new flame-resistant treatments. The first is THPOH, a durable flame-retardant treatment suitable for lightweight apparel-type fabrics. Both industry and the military are now evaluating THPOH on an advanced plant scale.

The second is a flame-retardant treatment for Cotton Flote that makes this improved cotton batting even better for use in automobile interiors, bedding, and upholstered furniture. Mattresses made from flame-resistant Cotton Flote went on the market this year.

The success of Cotton Flote has been hailed in the technical and trade press. The February 1968 issue of the Magazine Chemical Engineering contains a complimentary article about Cotton Flote with the interesting headline:

> "Cotton Padding a Threat to Rubber and Urethane Foams?"

It is indeed a switch when a natural product threatens synthetic products. This is the case of the man biting the dog. But it is very pleasing to the supporters of the natural products.

A new carbamate finish for durable-press cotton fabric was announced this year. In addition, the Polyset process is under advanced evaluation and nearing commercial adoption, as are some of the polymer treatments for durable press. Men's all-cotton, durable-press seersucker suits are scheduled for the market this summer, and production of similar seersucker for women's and children's apparel is planned later in the year.

Cottonseed is not so important economically as cotton fiber, but its importance is growing. We have had considerable success in processing both glandless and glanded cottonseed. There is great interest in the liquid cyclone process for manufacturing high-quality cottonseed flour from glanded seed for human use. Dorr-Oliver, Inc., has investigated the liquid cyclone process because of its potential both in the United States and abroad.

Other promising methods for processing cottonseed include air classification following hexane extraction, and extraction with selected polar solvents. Products made by these two techniques are being evaluated in cooperation with industry.

The results of our aflatoxin research continue to receive worldwide attention and are used to ensure that only high quality products enter food trade channels and to improve the quality of feed and food made from agricultural commodities including cottonseed.

Recent research in the SURDD on food products has led to results of commercial value. Microflake equipment for the production of orange crystals, based upon the foam-mat process developed by the Western and Southern Utilization Research and Development Divisions, has been installed in a Florida plant. Formalities leading to adoption of the bromate method as the official one for determination of citrus peel oil are proceeding rapidly.

Pure-culture fermentation of cucumbers, itself a major breakthrough, offers a new process for making pickles. It has been applied successfully to other vegetables and to green olives. A substance has been discovered in Manzanillo olives that inhibits fermentation. Its control through adaption of the pure-culture fermentation process should reduce losses and improve the quality of brined green olive products.

Progress in SURDD research was reported in 1967 in 247 technical papers and in 158 presentations before scientific and industrial groups. Thirty-nine patents covering SURDD inventions were allowed, and 10 licenses to use SURDD patents were granted. The SURDD was sponsor or cosponsor of 14 conferences attended by over 900 participants, exclusive of Division personnel.

The following members of the SURDD were honored in 1967 because of creative research:

> Ruth R. Benerito received the Federal Woman's Award for the distinguished service she has rendered to the profession of chemistry during the past 20 years as a brilliant research scientist and inspiring and untiring leader of research.
>
> Dr. Benerito also received the distinguished service award in the professional and scientific category from the New Orleans Federal Executive Association.
>
> A group in our Oilseed Crops Laboratory received the Department's Superior Service Award "For noteworthy research in the development of highly

effective water-resistant, fire-retardant paints applicable to civilian, industrial, and military needs." This group consisted of seven members: H. P. Dupuy, F. G. Dollear, L. A. Goldblatt, L. L. Hopper, E. T. Rayner, G. B. Verburg, and D. A. Yeadon. I am pleased to acknowledge that Mr. Hopper was a member of this group under a Fellowship supported by the Pan American Tung Research and Development League, one of the organizations that has provided financial assistance for our research.

I hope that you will agree with me that we have indeed had a busy and successful year.

I would like to express appreciation to everyone contributing to the success of this Conference. I wish to give special thanks to our General Chairman, Session Chairmen, speakers, visitors, and staff of the Southern Utilization Research and Development Division for the arrangements that have made this Clinic possible.

OPENING REMARKS

by

W. Smith
Plains Cooperative Oil Mill
Lubbock, Tex.

I guess it is not unusual for a farmer to be an honorary chairman of a cotton chemical research conference, as he is the one who ultimately benefits from the research. However, a farmer finds it a little difficult to speak and understand the language of the caliber of research scientists such as we have on this program. I can, however, understand that when the results of this research increase, the volume of cotton in turn increases my cotton market and my income.

Last year I told you that the cotton of the High Plains seemed to be so short it had only one end. This year I can tell you that, as a result of research, we have been able to increase our staple length at least one thirty-second. West Texas has produced historically for the export market, which causes me to be much more interested in research that deals with the domestic market; because, if we are to stay in the business and if programs are going to be geared to domestic production and domestic consumption, we on the High Plains need to get into the domestic market. Research of the type that has been done here is the only way we can get our short, coarse fiber into domestic markets.

I think it would be fitting and proper for each of you gentlemen who represent private industry to spend a little bit of your time and energy lobbying for the research appropriations pending in Congress, because through the coordination of private research and public research we will be able to solve the problems and keep ours a growing, thriving cotton business.

<ins>FIRST SESSION</ins>: J. L. Taylor, A. French Textile School, Georgia Institute of Technology, Atlanta, Ga., Chairman

EVALUATION OF CRYSTALLINE CHARACTERISTICS OF CELLULOSIC MATERIALS BY X-RAY DIFFRACTION
[SUMMARY]

by

V. W. Tripp
Southern Utilization Research and Development Division

Parameters which reflect the fine structure of cellulose and other polymers and which can be evaluated by X-ray diffraction include lattice dimensions, crystallite dimensions and orientation, and extent of crystallinity. Each of these aspects of the supramolecular geometry is pertinent to a description of the fiber material and how it is changed as a result of chemical and physical modifications. This presentation reports some of the results of investigations on a number of celluloses and related materials.

Crystallite orientation of single cotton fibers was examined by X-ray diffraction, and related to the molecular orientation observed by polarized light microscopy. The angle of orientation measured by these two methods was in fairly good agreement for a series of cottons with a wide range of "50 percent X-ray angles." It was concluded that the average angle of crystallite orientation in cottons can be represented by the "75 percent X-ray angle" obtained from a bundle sample.

The chemical modification of cellulose by the introduction of bulky side groups by etherification or esterification generally is accompanied by a loss of intensity of the original interferences and the appearance of new interferences. The intensity loss is greatest for the original (101) lattice spacing and like the growth of the new equatorial interference, is progressive with degree of substitution. The repeat distances of the new interferences have been compared with the size of the group introduced and, in general, show a reasonable correlation. The l-menthyl terephthalic acid ester of cellulose shows a spacing of 25 angstrom units, the largest thus far encountered.

Estimation of the absolute values of crystallite dimensions and degree of crystallinity involves problems of separation of the crystalline diffraction from background scattering arising from other sources. Using an arbitrary background separation, the length and breadths of the crystallites in cotton and other cellulosic fibers have been measured by the Scherrer line-broadening technique. The crystallite lengths and widths of cotton and the bast fibers (ramie, flax, hemp) are greater than those of the leaf fibers (kenaf, abaca, sisal). Regenerated celluloses, except for Fortisan, have smaller crystallite dimensions than native fibers. Mercerization of native fiber tends to reduce crystallite sizes, while acid hydrolysis appears to increase both dimensions. The apparent lengths of the hydrocellulose crystallites indicate the likelihood of chain folding.

Degree of crystallinity has been estimated by the Wakelin-Radhakrishnan correlation method, using a ramie hydrocellulose, a Fortisan hydrocellulose and a ball-milled cellulose as standards for crystallinity. Results on a variety of celluloses are presented. The technique has been applied to the estimation of accessibility of formaldehyde-crosslinked cottons to swelling agents such as NaOH of varying concentrations, ethylenediamine and trimethylbenzylammonium hydroxide. Crosslinking inhibits lattice conversion, although 20 to 30 percent NaOH solutions are apparently capable of disrupting crosslinks to a degree sufficient to permit extensive formation of cellulose II. All of the swelling agents significantly increase the "amorphous" fraction of the cellulose.

DISCUSSION

Comment: It is important to realize that the crystallite dimensions of cellulose calculated by the line-broadening technique are minimum values.

Mr. Tripp: We are attempting to estimate the extent of distortion by examining second reflection, but this is a difficult task.

APPLICATION OF GEL PERMEATION CHROMATOGRAPHY TO THE DETERMINATION OF MOLECULAR WEIGHT DISTRIBUTIONS IN CELLULOSIC MATERIALS

[SUMMARY]

by
L. Segal
Southern Utilization Research and Development Division

Gel permeation chromatography (GPC), also known as exclusion chromatography, restricted diffusion chromatography, molecular-sieve chromatography, and to the biochemist as gel filtration, is a means of separating dissolved polymer molecules according to molecular size or chain-length. The separation is readily accomplished mechanically and is a function of the retention time of the dissolved polymer molecules that have permcated a gel having a porous structure. The gel structure is made to have a graded range of pore sizes. The longer molecules are restricted in the extent to which they can permeate the gel structure; they are excluded by all but the larger pores. Shorter chains are less restricted by their lengths and spend longer periods of time in the gel before they are swept out by the flowing solvent.

Development of an automated instrument for performing the above separation was a significant advance in polymer science. In the commercially available chromatograph, a small volume of dilute polymer solution is injected into the flowing solvent stream which is pumped through the system at a constant rate. The concentration of the dissolved polymer in the solvent stream during the separation is measured by means of a flow differential refractometer, and the electronic output is plotted by a recording potentiometer or it can be punched onto paper tape for direct handling of the data by computer. The chromatograph columns, packed with beads of crosslinked polystyrene gel, are available in a wide range of pore sizes or permeability limits.

Fractionation of cellulose either as such or as a derivative to obtain molecular weight distributions has been carried out in the past, but the technique has been somewhat avoided, compared to the use of viscometry and other methods, because the operations are particularly lengthy, tedious, and subject to serious errors during the many manipulations involved. The capability of obtaining with GPC a plot of the differential molecular-weight distribution within some 2 hours, exclusive of sample preparation, opens a way for making chain-length distribution studies with cellulosic materials in a manner never before attainable.

The normalized, differential distribution curves obtained for nitrated celluloses I, II, III, and IV (prepared from a Deltapine cotton) show a rather broad spread of chain lengths, but are not markedly different from each other. There is, however, a definite increase of some 12 percent in the width of the curves of these particular preparations at half-maximum height going from cellulose I to celluloses II and III. The curve for cellulose IV showed a further increase for a total of 26 percent. This is all evidence of the extent of chain cleavage brought about by the treatments which end in lattice conversion. Very little difference in distribution was found between a regular acetylation-grade sulfite wood pulp and a nitration-grade sulfite pulp. Both of these, of course, were much broader than those of the cottons. An acetylation-grade cotton linters showed a distribution much sharper and narrower than the above pulps, while a Kraft high-alpha pulp showed a marked shift to shorter chain lengths with a still broader distribution.

Differential distribution curves for two hardwood pulps used for tire-cord rayon and two blends of hardwood and softwood pulps for textile rayon showed a very significant difference in the molecular chain lengths of the cellulose in the two types of pulps, but little difference within each type. Similarly, striking differences were observed among the curves obtained from purified cotton, purified cotton linters, and the sulfite and Kraft pulps mentioned above.

Treatment of cellulosic materials with strong acid causes extensive cleavage of the cellulose molecule, and prolonged treatment results in the leveling-off degree of polymerization (LODP). Differential distribution curves obtained so far on two cottons, one a Deltapine yarn and the other a commercial fabric, and their LODP hydrocelluloses indicate that the chain-length distribution in the hydrocelluloses is very much broadened over that of the cottons. The DP range for the hydrocelluloses is 10 to 10,000—three orders of magnitude—while that for the cottons is 1,000 to 100,000, or only two orders of magnitude. There is a striking close coincidence in the distributions of the cottons as well as those of the hydrocelluloses. The significance of this has not been established as yet.

DISCUSSION

Question: As your method of measuring DP shows a much higher level of DP, what would you say concerning what this shows relative to the straight-chain versus the chainfold concept that we heard of earlier this morning?

Dr. Segal: That is a very difficult question to answer in just a few minutes. The long chain-lengths that are indicated by the GPC data may not be valid. There are some indications in the literature based on conventional solvents that indicate that they may well be valid. But there are still arguments from the standpoint of the conformation of the molecules in solution. We don't know yet how big this trinitrate molecule is in relationship to the polystyrene standards that we use for calibrating the instrument. We are working on this now. We do know at present that tetrahydrofurane is thermodynamically a better solvent than ethyl acetate, and that ethyl acetate is better than acetone. Until we get a little more viscosity data with the polystyrene standards, we cannot very well answer the question as to the validity of the DP. As far as the chainfolding aspect is concerned, what we have to do is examine a series of samples where we have deliberately done something to the cellulose. We have a planned series of hydrolyzed samples where they were reacted 15 minutes, half an hour, and an hour. Here we will see what differences there are in the distribution of the chain lengths. Regardless of the magnitude of the DP's that we get at present, we can still form valid conclusions on the basis of the distribution curves that we get. If a chain folds regularly and we then hydrolyze the sample, we should get rid of all the amorphous material and we will begin to chop off the chain folds at the end of the crystallites. So then we would have little blocks. If, then, the chain is folded regularly, we should get a narrow distribution in these degraded materials. This is the concept that we are working on.

Question: How long does it take to run a sample in this type of operation?

Dr. Segal: It takes about 2½ hours from the injection of the sample to the disappearance of the dissolved-air peak. This, of course, does not include the time required for nitration of the sample.

Question: So you have to first make a derivative and then add 2½ hours' time to that?

Dr. Segal: Yes, that is correct; but, if you want to take a nitrate and go through the conventional precipitation fractionation procedure, you are going to find yourself faced with several weeks.

Question: Have you done any work trying to distinguish among the modes of damage in the cellulose using this technique? Oxidation versus hydrolysis versus microbiological damage?

Dr. Segal: No, but I am glad you brought that up. We have really just gotten started in this work with GPC in reference to cellulose. We also want to apply it to studies of crosslinking. There is a recent paper in Textile Research Journal showing that formaldehyde-crosslinked cotton can be nitrated and its DP determined. Perhaps you have seen that paper. We have some samples that Dr. Rowland has furnished us which is a series having a graded formaldehyde level. We are going to investigate that. I haven't really thought about working with oxidized material, but biologically degraded material, yes. I still want to hold Dr. Reese at the Army Natick Laboratories to his promise to furnish me with the proper cellulase.

Question: Have you done any work with

oxidized (from H_2O_2) or ozonated (O_3) cotton with your GPC apparatus, and if so, what were "typical" DP's?

Dr. Segal: In the letter to Dr. Kuryla it was stated that no work has been done with these materials. However, perhaps such work might be desirable in view of the extensive use of bleaches in laundering of cottons.

Question: Have you used any other solvents besides tetrahydrofurane? Our laboratory has used dimethylformamide and gotten some rather odd results.

Dr. Segal: No, we have not shifted to other solvents because of possible damage to the gel packing. We have to pick a solvent in which cellulose trinitrate is soluble and which is compatible with the column packing. Methyl ethyl ketone is one of these, but I have received some information that collapse of the gel packing is likely to occur when shifting to this solvent.

ESTIMATION OF PERMEABILITY, VOID SIZES, AND WATER BINDING IN COTTON

[SUMMARY]

by

L. F. Martin and F. A. Blouin
Southern Utilization Research and Development Division
(Presented by L. F. Martin)

Modification of the properties of cotton by crosslinking depends upon the accessibility of reactive hydroxyl groups of the polymer, under the reaction conditions employed, to reagents capable of introducing various forms of crosslinkage. The sizes of voids within the polymer matrix occupied by aqueous reaction media, and permeability to solutes of molecular sizes corresponding to those of the reagents used are controlling factors in carrying out the desired reactions. Estimates of the magnitude and distribution of voids and of the accompanying accessibility have been derived from numerous investigations by widely diverse techniques. A novel physical method of measurement based upon an application of the gel permeation technique, and the related determination of internal solvent volume at equilibrium, provide additional, independent estimates of accessibility. Results obtained by these means are considered in relation to estimates derived from physical measurements of density, X-ray diffraction, and gas adsorption, and from chemical measurements under swelling conditions by deuteration, periodate oxidation, and formylation.

Accessible hydroxyl groups are assumed to reside on surfaces and/or in the less ordered regions of the polymer structure, rather than in the highly ordered crystalline regions, and accessibility often is equated to the "amorphous," as distinguished from the crystalline polymer substance. The distinction is not unambiguous, and the estimates range from an aver-

age of only 8 percent by periodate oxidation to approximately 42 percent of accessible polymer by deuteration or moisture regain. X-ray measurements yield an average value of 27 percent. The differences are ascribed to the diversity of the molecular structural properties measured by the various techniques. X-ray diffraction measures the ordering of anhydroglucose units in the crystal lattice, whereas deuteration is a measure of the order of hydrogen bonding in the polymer structure.

When decrystallized cotton cellulose forms the medium in chromatographic columns, it exhibits properties similar to those of the graded dextran polymers used in gel permeation, from which solutes are eluted selectively in the order of decreasing molecular weights. The cellulose is swollen in the water used as the eluting solvent. Sugars and oligosaccharides of discrete, known molecular weights provide a range of molecular sizes of solutes from which estimates of the internal solvent volumes may be obtained by measurement of their elution volumes. Decrystallized cellulose has been found to have an internal solvent volume of 0.53-0.55 ml./g. by this method. A preliminary experiment on native cotton fibers, reduced by Wiley milling to a size suitable for use in a column, yielded values of 0.23-0.30 ml./g. Crosslinking of the decrystallized cotton with formaldehyde in reaction Forms W and D increased the internal solvent volume, while the bake-cure reaction (Form C) decreased the volume. The molecular weight limits of permeability also were altered by crosslinking; cellulose reacted in Forms W and V exhibited permeability to molecules of larger size, while reaction in Forms D and C reduced the maximum size of permeating solute molecules, in comparison with the uncrosslinked polymer.

The specific internal solvent volume may also be measured by immersing samples of cellulose in a solution containing a known concentration of a solute of sufficiently high molecular weight to be totally excluded from the internal voids. Stone and Scallan investigated the cell wall water volume of wood by this method, using dextran of average molecular weight 110,000 as the solute. The increase in concentration of the solution equilibrated with the wood samples relative to that of the known reference solution was determined polarimetrically, yielding values of approximately 0.4 ml./g. for unaltered, swollen wood cellulose. The internal volume was increased by Kraft pulping treatment in successive stages, up to a value of 1.21 ml./g. Good agreement was obtained between these measurements and determinations by the pressure plate technique at a relative vapor pressure of 0.9975 for their series of samples. Robertson, using the pressure plate method at a relative vapor pressure of 0.964, obtained a value of 0.23 ml./g. for the internal volume of cotton cellulose. This compares very satisfactorily with the internal volume of 0.19-0.22 ml./g. reported by Magne and others from determinations of nonfreezing water.

Measurements of internal volume and pore size distribution have been made by low temperature gas adsorption on cotton which had been swollen and then dried by solvent exchange. This method provides estimates of the internal surface area and of the distribution of total area within larger pores. Calculations of the surface area or internal volume distributed in pores of less than 25 Å diameter from the adsorption isotherms are of questionable value; however, it is possible that substantiation of the results might be obtained by comparison of gel permeation measurements with oligosaccharides having molecular weights of about 1000 to 1500 which permeate only the volume occupied by voids having diameters in the range of 20 to 30 Å.

Chemical methods such as formylation, periodate oxidation, and methylation have been used to estimate accessibility. These methods provide measurements of the accessibility of hydroxyl groups to attack by particular reagents which is not necessarily related to the internal solvent volume accessible to solutes. The data have been used by Warwicker to calculate percentages of disordered cellulose, ranging from only 6 percent by periodate oxidation to 28 percent by formylation, the latter being reported by Tarkow. Other workers obtained lower values, averaging 14.5 percent disordered cellulose estimated from their formylation data. If cotton decrystallized by ball-milling is representative of the fraction of disordered cellulose in the fiber structure, comparison of the internal volume of 0.53 to 0.55 ml./g. with the preliminary measurement giving at least 0.23 ml./g. for whole fiber suggests that a much larger percentage of the fiber cellulose is disordered, or, more probably, that accessible voids exist in other than disordered regions of the cellulose fiber structure.

DISCUSSION

Question: In many of the literature articles in which you read about the chemical reactions of cellulose, they say that a little bit of water must be present, and especially some reactions in DMF. Do you feel that there is any correlation between some of the work that you have done with water present, or if water is substituted, due to the fact that you need this water to effect the reaction?

Dr. Martin: If the question refers to possible correlation of the gel permeation measurements *per se* with the presence of traces of water, there is none unless the columns could be eluted with anhydrous solvent. Presumably the effect of traces of water present, in the reactions applied to the cellulose in non-aqueous media, e.g., DMF, upon permeation characteristics subsequently measured in columns eluted with water, was intended. We have not carried out any experiments along this line. Crosslinking by formaldehyde in the "non-aqueous" medium of Form D actually involves the presence of a substantial percentage of water introduced with the hydrochloric acid catalyst.

SECOND SESSION: J. P. Shealy, Jr., Graniteville Co.,
Graniteville, S. C., Chairman

WRINKLE RECOVERY PROPERTIES OF EASE OF CARE–TREATED COTTON FABRICS
[SUMMARY]

by
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(Presented by M. Kärrholm)

Systematic experiments of crosslinking cotton fabrics at different degrees of swelling were made on our previous project FG-SW-100. By applying the results in the new project FG-SW-108, we found that the value of the moisture regain should be within rather narrow limits in order to get both dry and wet recovery properties with higher values of the retained strength than that obtained by the conventional pad-dry-cure technique. The technique used is called moist-crosslinking and can be made at room temperature. It has been applied industrially in Sweden.

Further investigations on the USDA-project have been directed towards the dry wrinkle recovery properties of cotton fabrics subjected to different kinds of ease of care-treatments at conditions corresponding to those at actual wear of garments. Wrinkling and recovery normally occur simultaneously with moisture and temperature changes in the fabric, which is not taken into consideration in the usual test methods. We have tried to find out which conditions are critical for wrinkling behaviour and the response that different ease of care-treatments give to these conditions.

A cotton poplin fabric, desized, kierboiled, and bleached on industrial scale, called untreated (U) was subjected to the following laboratory treatments: Alkali setting (A) in 18-percent sodiumhydroxide solution, pad-dry-cure treatment (PDC) using dimethyldihydroxyethylene urea, drying at 80° C., to a residual moisture regain of about 6 percent and curing at room temperature at the same moisture regain, wet crosslinking (WC) also with the same resin, drying at 80° F. and then curing in a solution of hydrochloric acid and neutralizing. All fabrics were treated at controlled dimensions, washed, and stored for at least 14 days before testing. The fabrics were characterized by measuring dry and wet wrinkle recovery, tear strength, and nitrogen content.

The wrinkling properties have been investigated, using a modification of the conic wrinkling apparatus. The samples are randomly wrinkled and the moisture regain and temperature may be changed simultaneously by drawing conditioned air from special climate boxes through the wrinkled sample. After recovery in climate boxes the height of the wrinkles are determined and used as a measure of the recovery.

A preliminary investigation was made on (U)- and (PDC) fabric on the influence of wrinkling time and wrinkling load both at equilibrium and changing moisture conditions. After this the main experiments were carried out on all treatments comparing the wrinkling behaviour during increase of moisture regain, decrease of moisture regain, and at equilibrium regain. Further, the influence of temperature increase during wrinkling and decrease during recovery was studied.

Much more wrinkling is obtained during or shortly after changing the moisture regain compared to equilibrium conditions. Further cooling during recovery may decrease the recovery to a great extent. The sensitivity to moisture and temperature changes is very different for the different chemical treatments. The untreated (U), alkalisetting (A), wet-crosslinked (WC), alkaliset + pad-dry-cure (A+PDC) fabrics are all moisture sensitive, whereas pad-dry-cure (PDC) fabric is less sensitive and the moist-crosslinked (MC) fabric is almost uninfluenced by moisture changes.

It is well known that serious wrinkling of cotton fabrics may be obtained in the "half-dry" state of about 10 to 15 percent MR; occurring in practice, for example, at tumble drying. This might be caused by sensitivity to changing moisture rather than to a high degree of wrinkling at this moisture regain. An experimental series was made testing the wrinkling behaviour of cotton fabrics, chemically treated as described in the previous section. The fabrics were wet and while they were drying, creases were made in the fabrics at different moisture regains and the final recovery measured in standard atmosphere.

For comparison creases were made at different moisture regains at equilibrium conditions and the final recovery determined in standard atmosphere. These measurements were performed with a modified Monsanto technique. As a result, untreated cotton fabric (U), alkaliset (A), and wet-crosslinked (WC) show much better recovery of creases made at equilibrium than creases made during drying. The pad-dry-cure (PDC) and moist-crosslinked (MC) fabric are less dependent on the moisture conditions at creasing. This is in consequence with the results obtained in the previous section.

SURVEY OF PRELIMINARY RESULTS IN THE STUDY OF THE REVERSAL PHENOMENON IN THE FIBRILLAR STRUCTURE OF THE COTTON FIBER [SUMMARY]

by
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A preliminary report is given of the study of the "reversal" phenomenon in the structure of cotton fibers. This project is supported by the USDA under the P. L. 480 program and has been in effect for 3 years. Special attention has been paid to hereditary properties of the reversal phenomenon, the effect of environmental conditions on the reversal density (the number of reversals per unit length), the distribution of reversal distances, and the constraining effect of the boll wall on the free development of cotton fibers. During the next 2 years, more information will be obtained on the mechanical aspects of the structural features peculiar to the cotton fiber. The main part of the present report deals with the constraining effect exerted on the fibers during the growth period of the cotton boll.

In the first place, the author has attempted to relate the crimped form of the cotton fiber within the boll to the reversal density. Because of per unit fiber length—apparently more structural reversals are observed than crimps—the statement made by other research workers—that reversals are preferentially located at fiber bends—can be explained by suggesting that structural reversals are presumably the cause of the bend, rejecting as improbable the reverse situation.

Parallel to this, study material has been gathered to obtain as much variation as possible in cotton boll volume by including different types of cotton. Next to the boll volume, fiber weight per unit volume, seed index, and percentage of lint have been taken into account.

In addition to this investigation, the growth space has been modified artificially within a definite cotton type through the application of controlled pollination. Space available and space used by the growing hair have been measured for a large number of bolls, where the number of seeds varied from 1 to 33. A degree of hindrance has been calculated. From these observations it could be deduced that, although the fiber mass has the opportunity to develop in a larger space, it remains constricted to the neighborhood of the seed on which it grows. None of the measured volumetric features of the cotton boll could be related to the reversal density. Therefore, the conclusion is suggested that apparently the external constraint of the boll wall against the fiber assembly could not be the cause of generation of structural reversals.

The opinion that the reversals phenomenon observed on the cotton fiber is inherent to the growth may, therefore, better withstand criticism than any other hypothesis.

Based upon the reversal distance distribution a brief description is given of a suggested fiber growth model. This model consists essentially in the hypothesis that the length-wise growth of the fiber is activated by annular growth units originally present in the primary wall; the development of which defines the entire growth matrix of the secondary layers within the structural units.

When the development of the original growth unit happens to be oriented towards the hair base, the disposition of the secondary layers has an S-shaped fibrillar structure. An orientation towards the hair tip generates a Z-shaped fibrillar structure in the deposition of the secondary layers.

Finally, first results are given about the mechanical properties of reversals. A special apparatus has been designed and constructed to make, on a single fiber, multiple tests with zero gage length at predetermined locations along the fiber. Applying this new technique it appears that, because of the tapered form of the fibers, special attention must be given to the sequence of test repetitions on a single fiber to obtain unbiased strength values.

The first results have shown that the structural reversals are really weak places and that the loss in strength because of the presence of reversals may be estimated to be at least 15 to 30 percent depending upon the samples tested.

Future work in this field will consist in investigating whether current or special fiber treatments may affect, in one way or the other, the loss of strength at reversals observed on untreated fibers. Among the treatments already examined, such as boiling, bleaching, mercerizing, steaming, and drying, it appears that only the last two treatments decreased the strength level in a more pronounced way at reversals than between them. A definite conclusion in this field can only be given after completion of the entire program.

DISCUSSION

Question: What about the elongation properties of the fiber at reversals and between reversals?

Dr. Fransen: The special measuring device described in the paper has been set up to evaluate tensile strength of the fiber at a given predetermined position; therefore, the technique applied uses a zero gage length. The microscope serves only the purpose of putting the fiber in the exact position on the stage. Covering the fiber with clamps and inclining the stage for loading the fiber make any use of the microscope for observing elongation of the fiber impossible.

THE ACTION OF ALKALINE AND ACID SWELLING AGENTS ON THE FINE STRUCTURE OF COTTON

[SUMMARY]

by

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The swelling of scoured cotton in sodium hydroxide is well known and is the basis of the mercerization process. At 25° C., the cotton achieves a maximum degree of width-swelling (DSw.) in 4N sodium hydroxide, and only at 0° is this exceeded in 3N sodium hydroxide with the rupture of the primary wall. At 100° the maximum DSw. is 1.2 and the limit set by the primary wall is not attained in any concentration.

When an iron tartrate complex (EWN) is dissolved in 2N sodium hydroxide containing free sodium tartrate, the swelling attained depends on the concentration of the EWN. In 100 g./1 EWN at 25° C., the degree of swelling is similar to that found with 4N sodium hydroxide, but unlike swelling in sodium hydroxide, there is no evidence for intrafibrillar swelling, and, therefore, the swelling must be produced by interfibrillar swelling alone. Above 100 g./1 EWN the cotton will partially or wholly dissolve in the swelling agent if left long enough. Evidence for intrafibrillar swelling is then found.

The swelling behaviour in acids is more complex and other side reactions can take place. In sulphuric acid at 25° C. cotton can swell without solution in concentrations up to 63 w percent, after which solution and decomposition takes place. In 62 w percent acid the DSw. is similar to that in 4N sodium hydroxide but no evidence for intrafibrillar swelling is given.

Phosphoric acid swells cotton at 25° C. in concentrations up to 81 percent, and between 83 to 95 percent at all other concentrations solution takes place. The behaviour in the first range of concentrations is similar to that in sulphuric acid and only interfibrillar swelling is detected. In the second range of concentration, both interfibrillar and intrafibrillar swelling takes place, and in this respect the swelling behaviour of cotton resembles that in sodium hydroxide solutions. The values for the DSw. in 80 and 90 percent phosphoric acid are very similar but the swelling mechanisms to achieve this is different.

Nitric acid presents an even more complex system. Swelling takes place at 25° C. in concentrations up to 80 w percent and in concentrations between 86 and 100 percent, but solution is found in concentrations between 80 and 86 percent. The curve for the plot of the DSw. against concentration shows a minor peak with a DSw. of 1.26 in 65 percent acid.

Up to this point mainly interfibrillar swelling is detected, but in 68.8 percent acid the DSw. falls to 1.2 and X-ray analysis reveals the presence of the Knecht compound thus indicating that penetration of the fibrils had taken place. In higher concentrations up to 80 percent the DSw. rapidly rises until solution takes place. Cotton in nitric acid of concentration between 86 and 100 percent swells, but the degree of swelling falls with the rise of concentration, and rapid nitration confuses the interpretation of the results.

A few experiments have been carried out with perchloric acid at 25° C., but rapid oxidation of cotton can take place in higher concentrations of the acid and this restricted the work. A DSw. of 1.14 was found in 60 percent acid and partial penetration of the fibrils was detected: swelling appeared to be less in higher concentrations of the acid. Sufficient work to substantiate this has not been carried out.

These experiments showed that the degree of swelling as measured by width changes is not sufficient to describe the character of the swelling process, since the same DSw. can be achieved either by interfibrillar swelling alone, or by a combination of interfibrillar and intrafibrillar swelling. The change in the fine structure of cotton brought about by swelling agents is, therefore, dependent not only on the degree of swelling achieved, but also on the type and concentration of the swelling agent employed.

The properties of the cotton after immersion in the swelling agent under standard conditions, washing, and drying in the air, indicate the nature of the changes in the fine structure brought about by the treatment.

Accessibility to water vapour can be deduced from moisture regain values, and an increase in the accessibility over that produced by swelling in water alone was only found where the swelling agent had produced intrafibrillar swelling during the treatment. Retention of liquid water was also higher if intrafibrillar swelling had taken place, although an exception was found with phosphoric acid which produced high water retentions in the treated cotton although only interfibrillar swelling had taken place.

Infrared-deuteration measurements, which measure hydrogen-bond order, correlated with moisture sorption results and showed only appreciable increases in hydrogen-bond disorder for those samples swollen under conditions in which intrafibrillar swelling had taken place.

Levelling-off degrees of polymerization (LODP) measured on residues from acid hydrolysis experiments gave values around 140 for the LODP if interfibrillar swelling only had taken place, a value similar to that for untreated scoured cotton. If intrafibrillar swelling had been achieved during the swelling treatment then LODP values around 60 were produced, and intermediate values were given if only a partial change in lattice was found, indicating incomplete intrafibrillar swelling. Some results suggest that LODP values depend on the accessibility of the sample to aqueous acids and not on the so-called crystallinity of the sample.

However, in reagents that do not appreciably swell the structure during the reaction quite different effects are found. Thus, the rate of acetylation, expressed as A percent per 24 hrs, in an acetic anhydride/pyridine solution is 7.6 for scoured cotton, and only 0.6 for cotton treated in 5N NaOH. In general, swelling reagents that cause intrafibrillar swelling reduce the acetylation rate dramatically, but those that only produce interfibrillar swelling can increase the acetylation rate. It is thus important to choose the swelling conditions carefully if subsequent chemical reaction is to be carried out on the treated cotton.

Physical measurement of lateral order by X-ray methods measures the disorder in position of the atoms as well as changes in size of the regions diffracting the X-rays. If interfibrillar swelling alone was attained during the treatment then little change in X-ray lateral order was found, but if intrafibrillar swelling took place greater disorder was detected in the structure especially in the (101) planes.

It is concluded from these studies that if cotton products are to be improved by the treatment of the cotton by swelling agents, the conditions and type of swelling agent need careful selection according to the improvement required.

DISCUSSION

Question: Have swelling techniques been used to show whether crosslinks are intrafibrillar or interfibrillar?

Dr. Warwicker: No, this has not yet been done.

Question: What effects would be expected in commercial mercerization if fabric were treated with (a) steam; (b) hot water; (c) cold water, to wash out caustic?

Dr. Warwicker: Before answering the question, I will point out that the fabric construction restricts swelling; therefore, effects are not as pronounced as when treating loose fiber. With regard to the question, we have no information on the effect of steam. If hot water is used to wash out the caustic, the product will have the cellulose I structure; but if cold water is used, part of the crystalline fraction will be cellulose II but there will also be some cellulose I because of constriction due to fabric construction.

COMPOSITION AND FINE STRUCTURE OF COTTON FIBERS GROWN IN CONTROLLED ENVIRONMENTS

by
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ABSTRACT

Deltapine cotton grown under continuous illumination and at controlled temperatures was harvested at intervals from 20 days after blossoming to boll opening. Fiber maturity and composition, cellulose crystallinity and accessibility, and response to differential dyeing were measured. In open bolls the X-ray crystalline index increased with increasing average daily temperature. Rate of fiber maturation, whether measured by observation under polarized light or by changes in cellulose and sugar content, was temperature-dependent but in a complex manner. Accessibility of the fiber cellulose, as measured by iodine sorption, dye sorption, and enzymatic attack, was very high in young fibers and decreased as the fibers matured. Rate of decrease in accessibility was much lower when bolls had been grown at low temperatures.

INTRODUCTION

The work to be described in this report was carried out in the Plant Fibers Pioneering Research Laboratory while the author was a member of that group. It is being continued in the Cotton Physical Properties Laboratory. The purpose was to examine the effect of temperature during growth of the cotton fiber with respect to the crystallinity and accessibility of the cellulose in the fiber. These properties were to be measured at various stages of fiber development including the mature boll.

By way of background a few previous studies will be cited. Berkley and Kerr (1) published X-ray photographs showing little or no crystalline cellulose in fibers removed from unopened bolls and kept moist. Heyn (4) later reexamined this question and demonstrated some crystallinity by X-ray diffraction. Nelson and Mares (6) studied the crystallinity, accessibility, and lateral-order distribution of field-grown cotton at various stages beginning at 15 days after blossom and found progressive increases in crystallinity and decreases in accessibility as fibers matured. Grant and Orr (2) compared the physical properties of mature fibers grown under several schedules of constant or variable light and temperature, and found only small differences, mostly due to the percentage of mature or thick-walled fibers in the sample.

The data to be presented here are mostly descriptive at this stage of the study. They will show how certain properties change with the stage of boll development. The correlation of these properties with the temperature of growth is only partly accomplished at the present time, but it is continuing.

Experimental.—Cotton was grown at the Texas A&M University, under a research contract directed by Robert Powell, in special environmental chambers in which both temperature and light could be closely controlled. In table 1 the conditions of growth and time of harvest are shown. Deltapine 14 variety of American Upland Cotton was chosen as suitable since previous experiments had shown it to grow reasonably well under the special conditions to be used. All cotton was grown under continuous light (that is, 24 hours a day) in order that the variation due to this environmental condition would be minimized. Seven series of cottons were grown under different temperature schedules. Three series were grown at constant temperatures (90°, 80°, and 70° F.) Temperature was alternately high (15 hr.) and low (9 hr.) for four series (90° to 70°, 80° to 70°, 90° to 60°, and 80° to 60° F.) The 60° level was included because cotton fibers practically cease to grow at this temperature. Bolls were harvested at specified days after blossom as shown in the table. The 90° series developed so rapidly that a very early harvesting was made at 12 days and the last date of harvest was 30 days, since the bolls began to open on the plants at approximately 33 days. In the other series, harvesting was at 5-day intervals, from 20 to 40 days, with the exception of the 70° series in which the bolls were growing so slowly that one additional collection date before boll opening was instituted. Upon harvesting, immature bolls were de-hulled. Two locks of each boll were freeze-dried (frozen in liquid nitrogen and dried in vacuum chamber). The other two (or three) locks were preserved in methanol.

The properties that were observed or measured on the freeze-dried material are listed below. (The methanol-preserved series has not yet been studied.)

Table 1.—Conditions of growth and time of harvesting of Deltapine-14 cotton grown in environmental chambers under continuous light

Temperature °F	Schedule hour/day	Bolls harvested and freeze-dried							Open bolls
		Number of days after blossom							Number of days to open
		12	20	25	30	35	40	49	
90	24	X			X				33
80	24		X	X	X	X	X		40
70	24		X	X	X	X	X	X	54
90 to 70	15-9		X	X	X	X	X		45
80 to 70	15-9		X	X	X	X	X		43
90 to 60	15-9		X	X	X	X	X		57
80 to 60	15-9		X	X	X	X	X		60

PROPERTIES MEASURED

Open bolls:

- Boll period (days to open) (Powell)
- X-ray crystalline index

Open bolls and freeze-dried immature bolls:

- Fiber maturity count
- Moisture regain at 65 percent relative humidity
- Cellulose and sugar content
- Iodine sorption
- Dye sorption
- Enzyme accessibility

The boll period or average number of days for the boll to open on the plant was supplied by Dr. Powell. X-ray crystalline index was obtained by the Wakelin correlation technique (9). Fiber maturity counts were made by the American Society for Testing Materials microscopic method which employs polarized light and selenite plate. Moisture regain at 65 percent relative humidity was determined on samples which were dried over phosphorus pentoxide and then exposed in constant-humidity chambers. It is expressed as percentage of moisture based on the dry weight of the sample. The cellulose and sugar contents were determined on a semimicro scale by a modification of the technique of Hessler and Power (3). Dye sorption was determined by a substantially modified version of the Rebenfeld and Wu (7) technique for quantifying the Goldthwait dye test. The essential modifications were dyeing at room temperature, the addition of a third dye of molecular weight intermediate between those of the red and green dyes employed in the Goldthwait technique, and the use of semimicro samples because of the small quantity of material available. Enzyme accessibility was also determined on semimicro samples, by incubating the purified fibers in a solution of the cellulase prepared from *Trichoderma viride* and measuring the sugars produced.

Results and discussion.—Figure 1 shows the relation between the average boll period and the temperature at which the plants were grown. A trial plot of the average daily temperature produced only a rough correlation; by calculating the degree-hours at and above 70° F. the data in figure 1 were obtained. This was done because it is known that cotton essentially stops growing at a temperature of 60°. By omitting the hours at 60°, we obtained a better correlation.

Figure 2 shows the correlation between the X-ray crystalline index and the average daily temperature. In this case the average daily temperature yielded a better linear relation than did the degree-hours at 70° and above. Except for one point, that for the fibers grown at 80° for which series many types of data were anomalous, we find a rather good relation between the crystallinity index and the average daily temperature. This correlation is for the open bolls only. Crystalline indices for immature fibers have not yet been measured.

The increase in percentage of mature fibers with the age of the immature boll is shown in figure 3. Data for "mature" bolls—those that opened before harvesting—are shown as the last point on each curve. No attempt has been made to correlate the data with temperature at

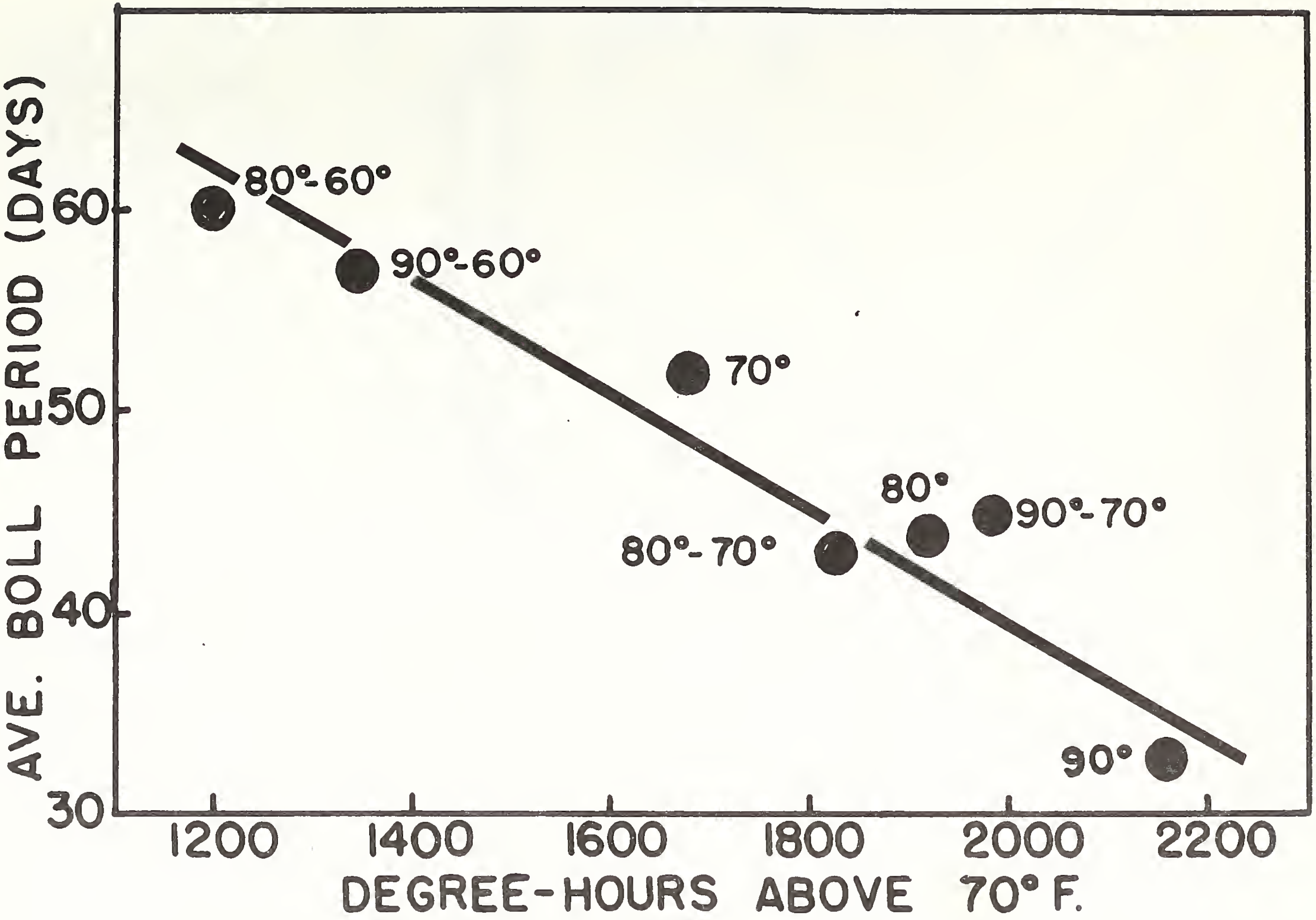

Figure 1.—Relationship between average age at which bolls opened (boll period) and degree-hours at and above 70° F.

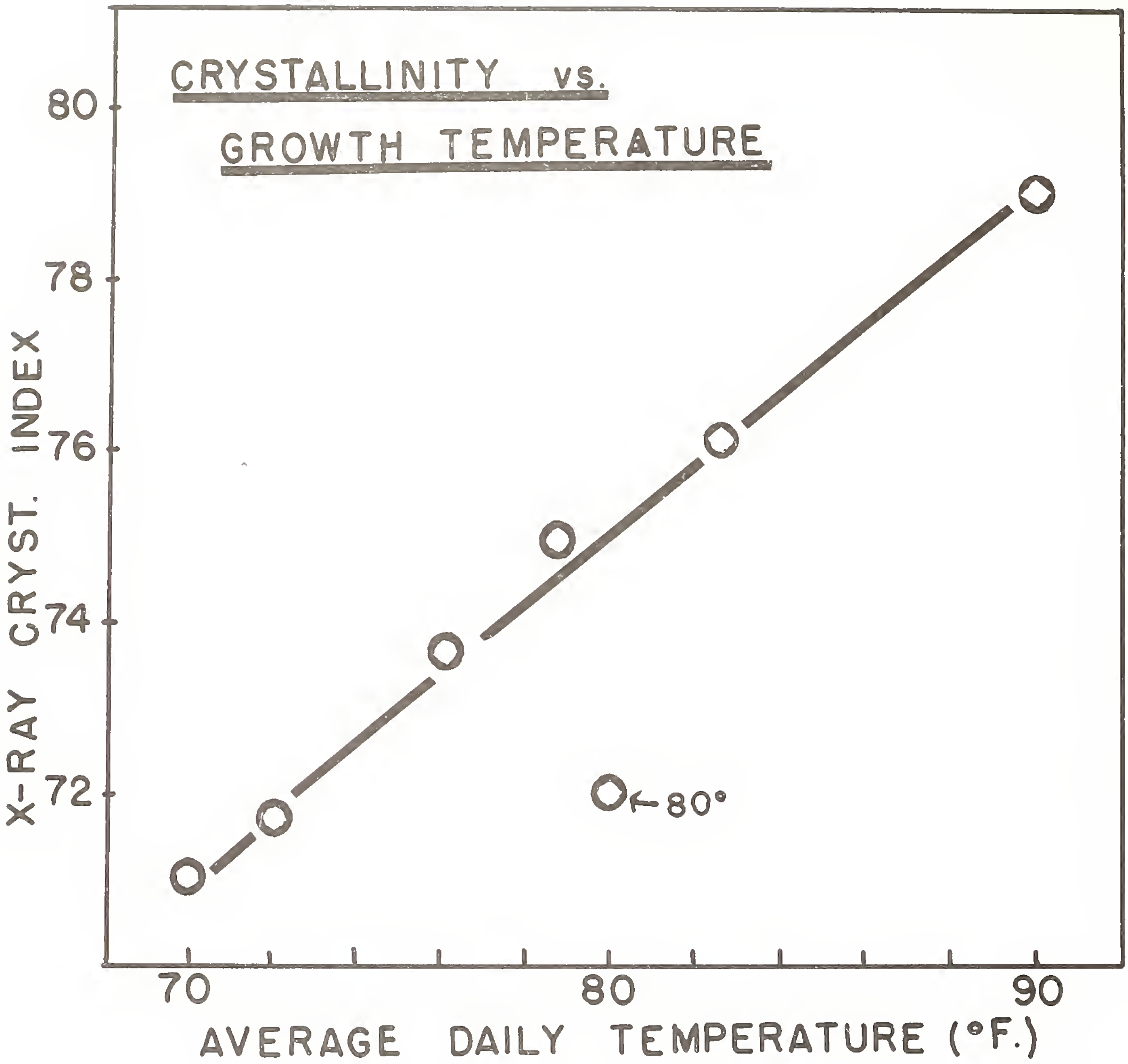

Figure 2.—Relationship between X-ray crystalline index of fibers from open bolls and average daily temperature.

this stage. It will be noted that the series grown at 90° matured very rapidly as shown by the fiber maturity count. The series grown at 70° matured very slowly and never reached the same level of maturity as those grown at higher temperatures. The other series matured at intermediate rates. It should be noted that the 80° to 60° series developed at about the same rate as the 70° fibers, whereas the 80° to 70°, 90° to 70°, and 90° to 60° series matured at rates approaching that of the 90° series. Anomalous data for the 40-day and open-boll samples of the 90° to 70° series are undoubtedly due to some uncontrolled factor in growth of these bolls.

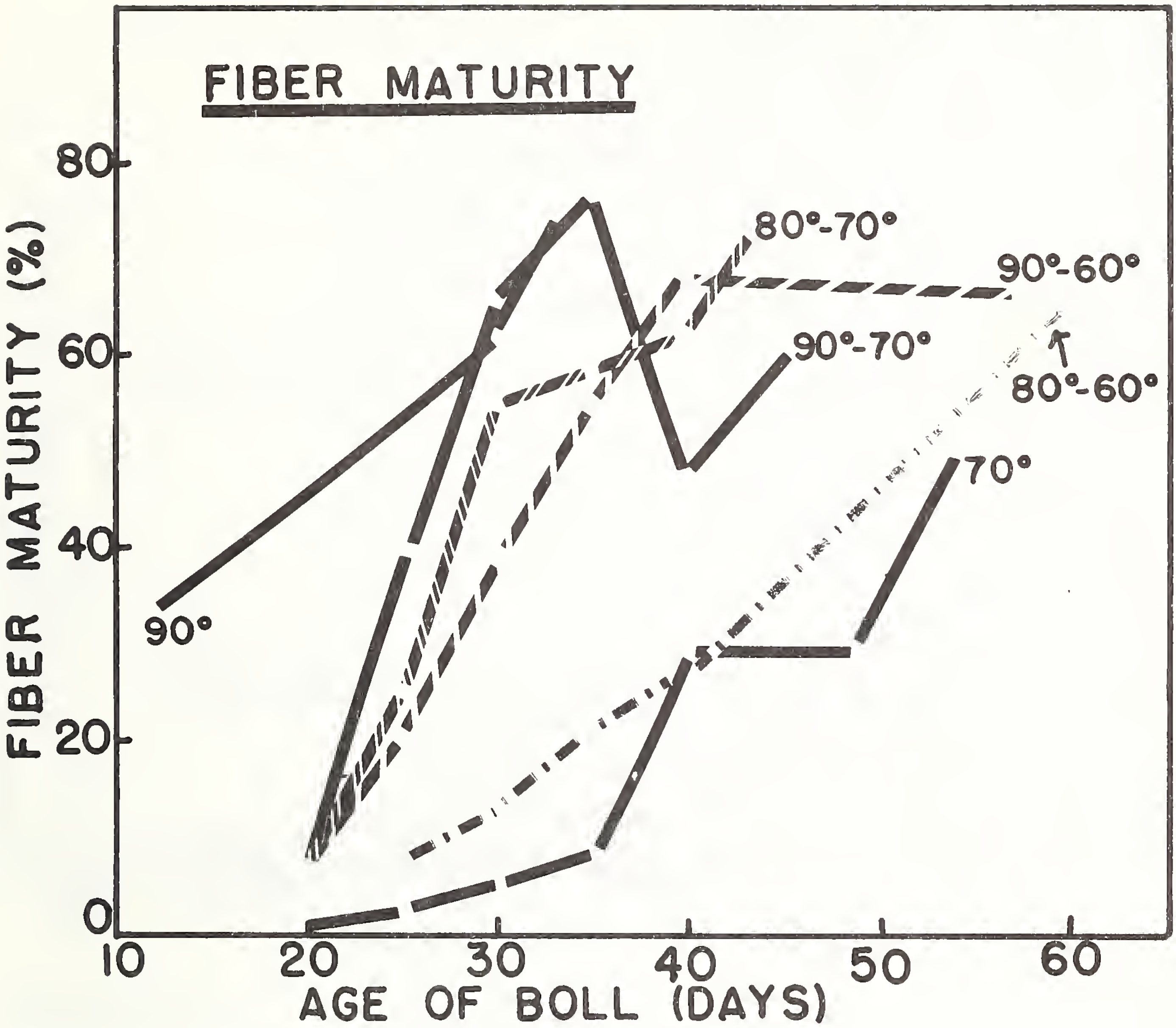

Figure 3.–Changes in fiber maturity count (by polarized light) with age of boll. (Ends of curves represent open bolls.)

Compositional data are given in figure 4. The percentage of cellulose increases for all series as the percentage of sugars decreases, as would be expected. The fibers grown at a constant temperature of 90° developed cellulose very rapidly and the sugar content decreased very rapidly, paralleling the maturity count. The fibers grown at 70° or at alternating temperature of 80° to 60° developed cellulose quite slowly and had very high percentages of sugars even up to shortly before boll opening. The other series were intermediate.

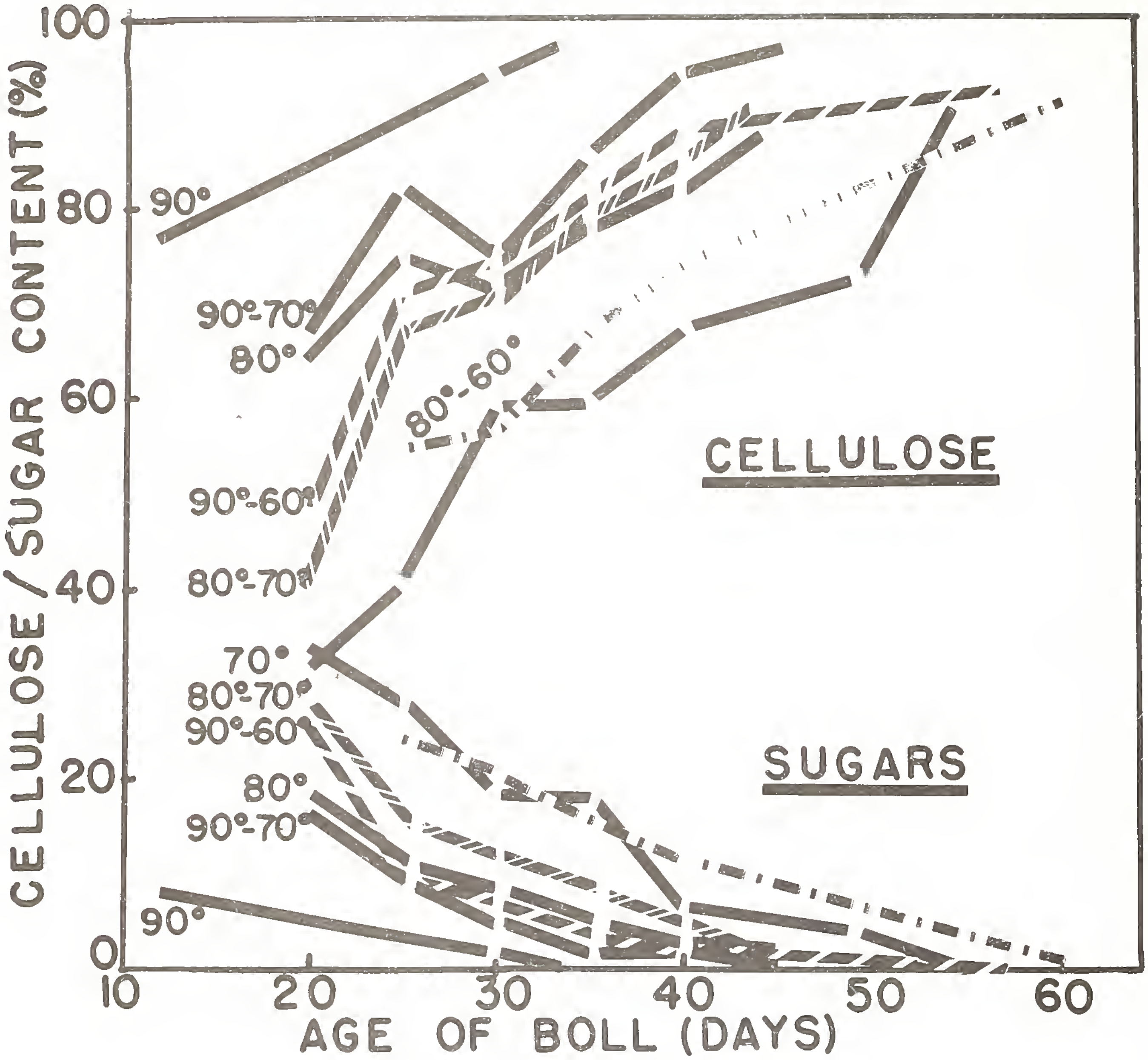

Figure 4.—Changes in cellulose and sugar content with age of boll. (Freeze-dried fibers and fibers from open bolls)

The moisture regain values at 65 percent relative humidity are given in figure 5. Data under standardized conditions were available for only four series. Note that these moisture regains were determined on the raw cotton; therefore, the very high values for the 20- and 25-day bolls reflect the hygroscopicity of the noncellulosic constituents, specifically, sugars and pectic substances.

Iodine sorption data are given in figure 6. Iodine sorption is one method of measuring the relative accessibility of cellulose. As shown in figure 6, the young fibers have a high accessibility which decreases as the fibers develop. This trend is the inverse of that of the maturity count. The 90° material decreased most rapidly in accessibility as measured by iodine sorption, and the 70°

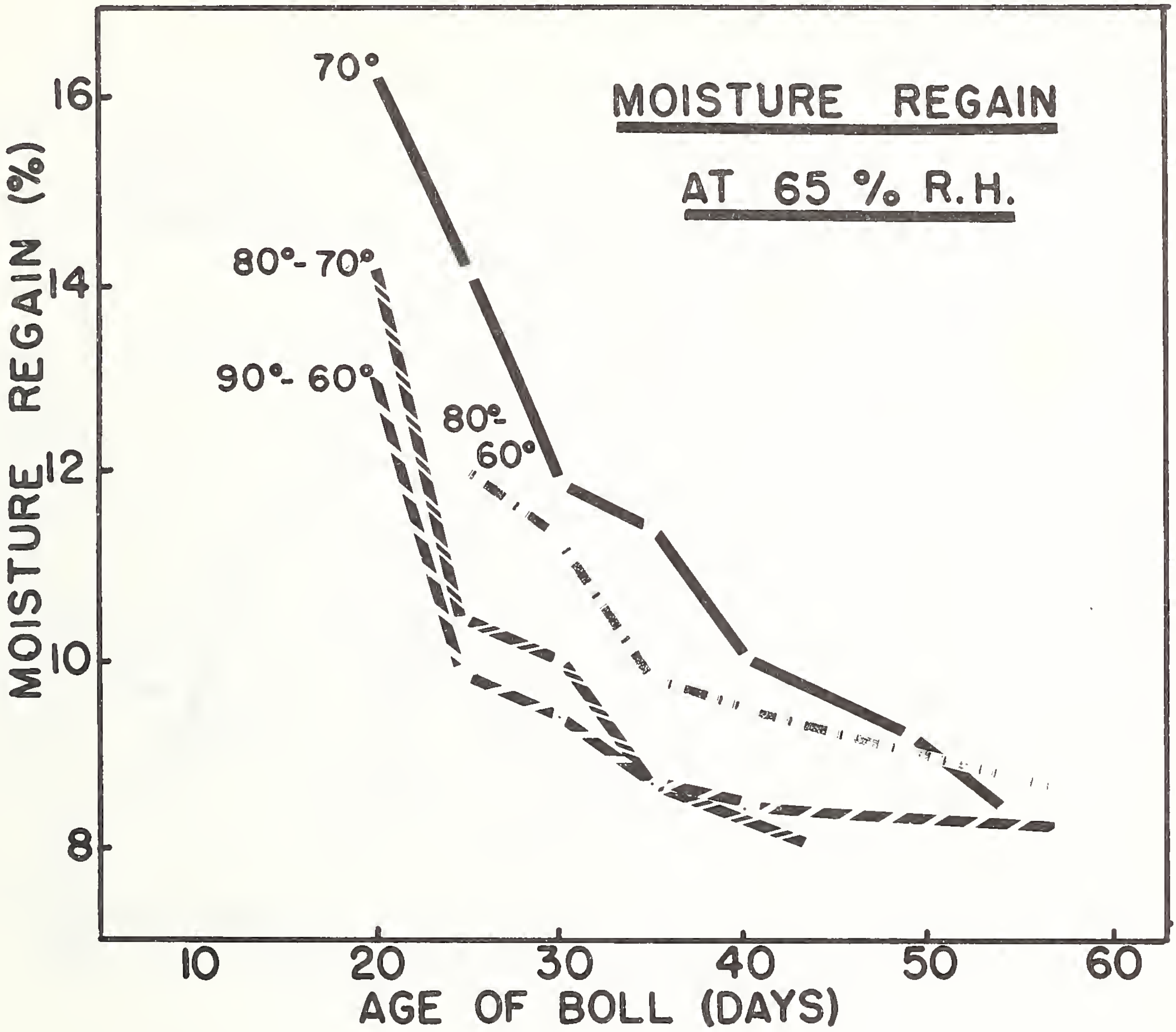

Figure 5.—Moisture regain at 65 percent R.H. of freeze-dried fibers of various ages and of fibers from open bolls.

and the 80° to 60° material decreased most slowly. The other series fell in between. The dye sorption data shown in figure 7 are a slightly different type of accessibility measurement. The dye molecules were chosen for their molecular size. In this particular instance, we found that only the largest molecule (the green dye of the Goldthwait dye test) showed substantial differences among samples in the several series. Therefore only the data for the sorption of the green dye (in milligrams of dye per gram of dry fiber) are presented in figure 7. Because of interferences by the natural color in the fibers in the spectrophotometric determination of the dye content, these fibers were purified by extraction with 2-aminoethanol before dyeing but were kept wet until placed in the dye bath. Dye sorption

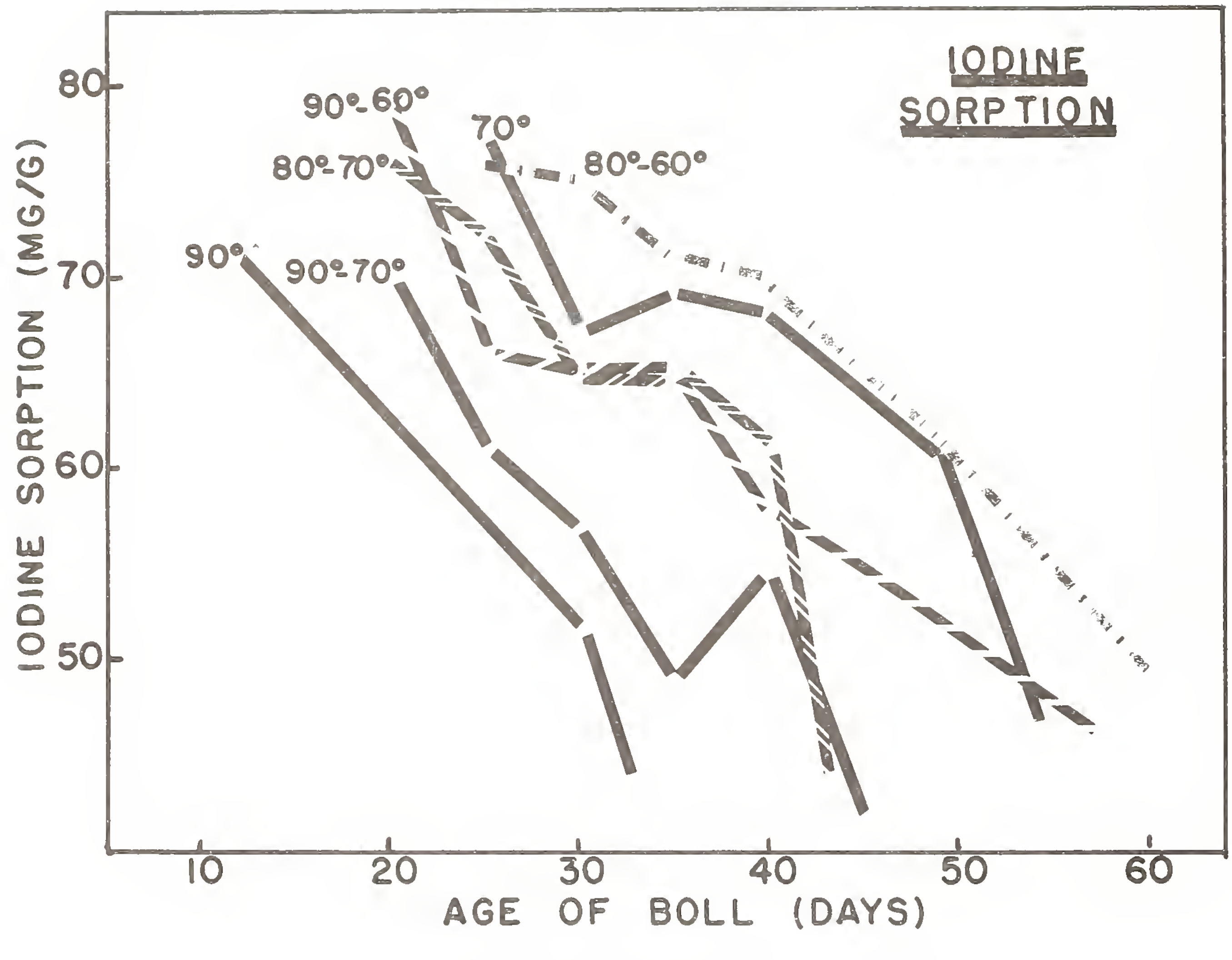

Figure 6.–Iodine sorption of freeze-dried fibers and fibers from open bolls.

was very high in the youngest, most immature fibers (70° and 80° to 70° series), somewhat less for the 90° to 60° and 90° to 70° series, and quite low for the youngest fibers of the 90° series. Dye sorption decreased rather rapidly with age of boll, more rapidly than iodine sorption did. Fibers from open bolls had about the same dye sorption regardless of growth temperature.

Enzyme accessibility is a new type of measurement of accessibility which we are introducing. In most studies the cellulose substrate has been used as a test medium for determining the activity of various enzyme preparations. The work of Mandels and Reese (5) and of Selby and Maitland (8) have shown that the enzyme complex prepared from Trichoderma viride can continue to attack cellu-

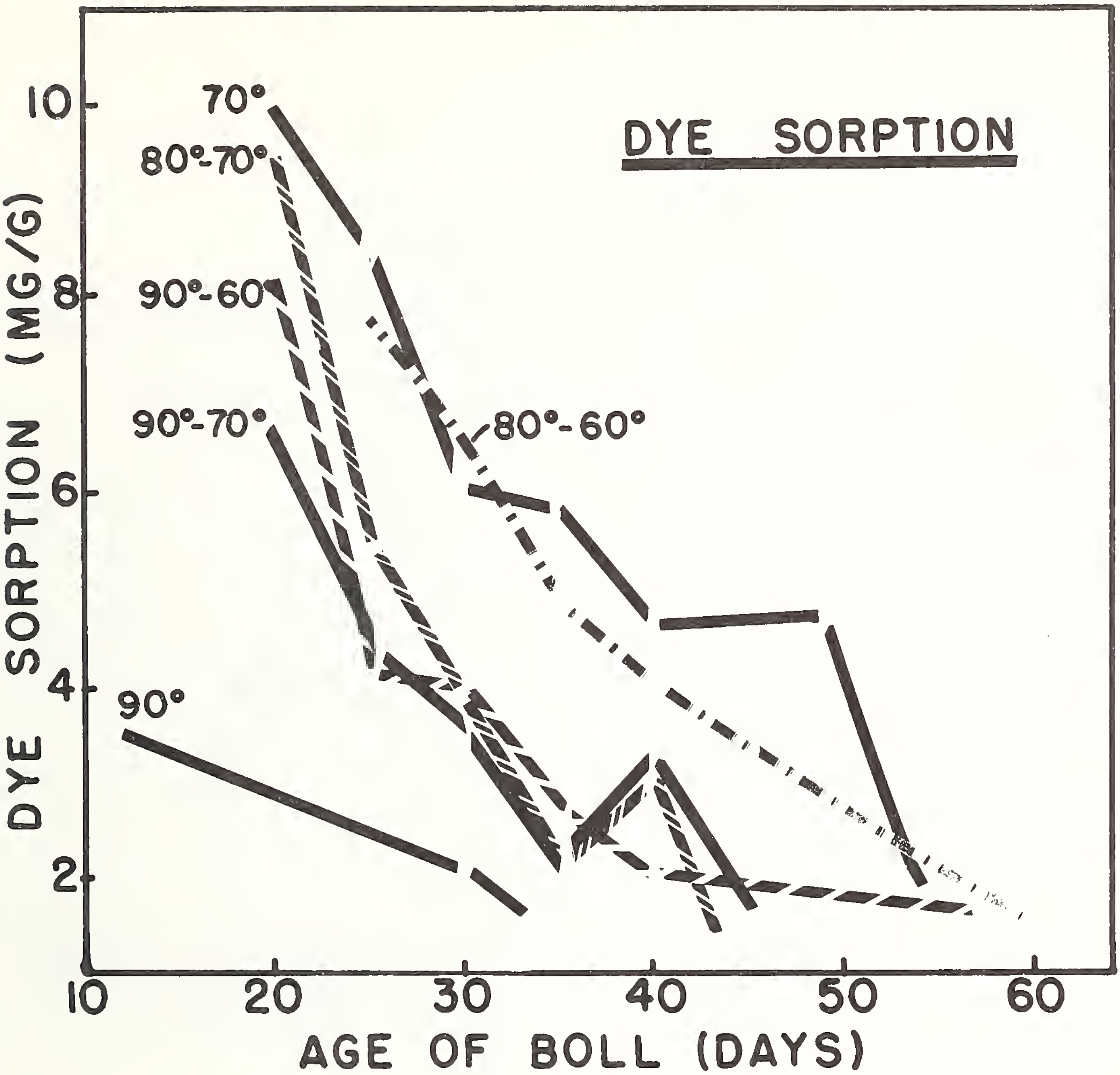

Figure 7.—Dye sorption of freeze-dried fibers and fibers from open bolls.

lose in the absence of the micro-organism itself. This is attributed to the presence of a component which by itself cannot attack cellulose but which is synergistic with the cellulolytic enzyme. In our test we purified the fibers, washed them thoroughly, and maintained them in the wet condition. Then we incubated the fibers with a standard buffer solution of the cellulase at a fixed temperature and for a fixed time. The extent of attack was determined by the percentage of sugar produced. Figure 8 shows the sugar produced by this standardized test for the various series. Again, it is seen that in general at an early age the fibers are very accessible but as the age increases, that is, as the fibers mature, the accessibility to attack decreases, being the least for the fibers from the open bolls.

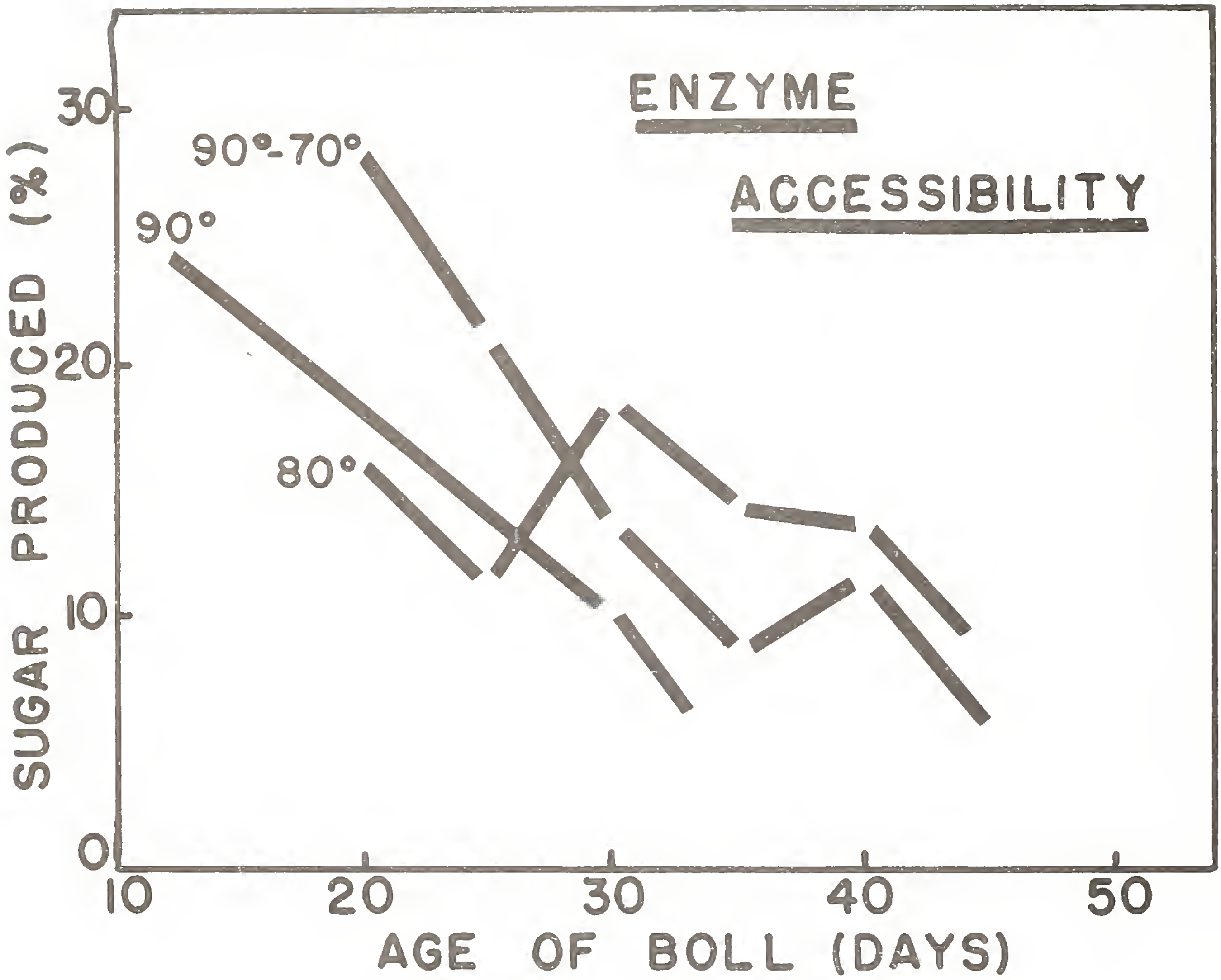

Figure 8.–Accessibility to enzyme from T. viride, as measured by sugar produced.

Figure 9 shows the relation between dye sorption and the polarized-light fiber maturity count. As would be expected there is a general correlation. It is not a linear correlation, and the plotted values show considerable scatter. Fibers from open bolls (shown as open circles) absorbed nearly the same amount of dye, regardless of maturity count.

Correlations between temperature of growth and the properties of the immature fibers have been only partly explored. No simple relationships were found. Further examination of the data is in progress.

In summary, the data illustrate that the primary effect of temperature is to regulate the rate of fiber maturation. The

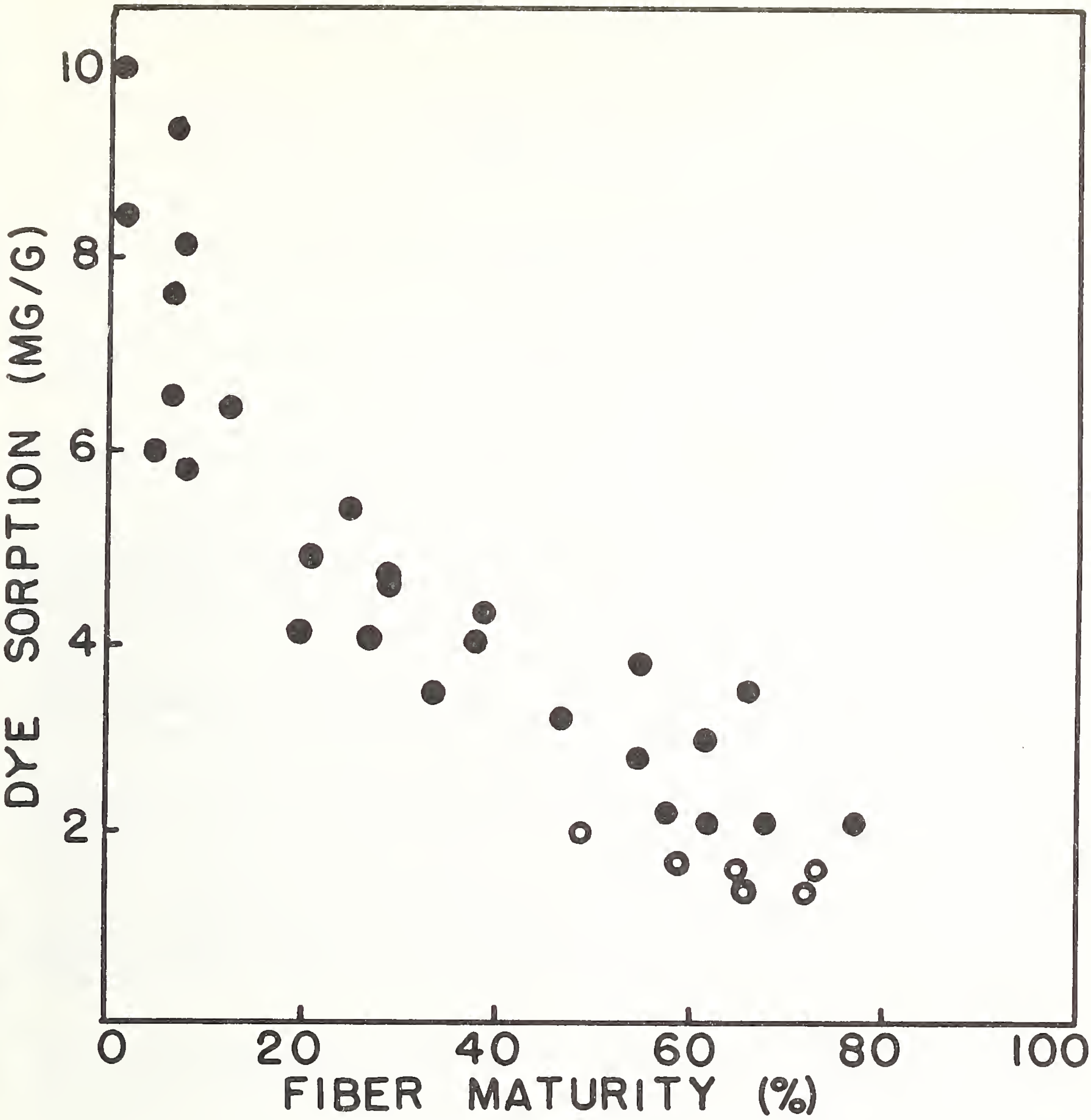

Figure 9.—Relationship between dye sorption and fiber maturity count. Open circles are fibers from open bolls.

differences in accessibility between young or very immature fibers and older, more mature fibers are quite large, whether determined by iodine sorption, dye sorption, or enzymatic attack. Interrelationships between accessibility, crystallinity, and the physical properties will be discussed in future reports on these investigations.

REFERENCES

1. Berkley, E. A., and Kerr, T. 1946. Structure and Plasticity of Undried Cotton Fibers. Indus. Engin. Chem. 38: 304-309.

2. Grant, J. N., and Orr, R. S. 1966. Cotton Fiber Structure and Physical Properties Altered by Environment. Textile Res. Jour. 36: 432-440.

3. Hessler, L. A., and Power, R. E. 1954. The Use of Iodide Absorption as a Measure of Cellulose Fiber Crystallinity. Textile Res. Jour. 24: 822-827.

4. Heyn, A. N. J. 1965. Crystalline State of Cellulose in Fresh and Dried Mature Cotton Fiber from Unopened Bolls as Studied by X-Ray Diffraction. Jour. Polymer Sci., Pt. A, 3:1251-1265.

5. Mandels, M., and Reese, E. T. 1964. *In* Developments in Industrial Mycology, Vol. 5; 5-20. American Institute of Biological Sciences, Washington, D. C.

6. Nelson, M. L., and Mares, T. 1965. Accessibility and Lateral Order Distribution of the Cellulose in the Developing Cotton Fiber. Textile Res. Jour. 35: 592-603.

7. Rebenfeld, L., and Wu, H. 1961. A Quantitative Study of Differential Drying of Cotton as a Means of Elucidating Fiber Structure. Textile Res. Jour. 31: 886-892.

8. Selby, K., and Maitland, C. C. 1967. The Cellulase of *Trichoderma viride*. Separation of the Components Involved in the Solubilization of Cotton. Biochem. Jour. 104: 716-724.

9. Wakelin, J. H., Virgin, H. S., and Crystal, E. 1959. Development and Comparison of Two X-Ray Methods for Determining the Crystallinity of Cotton Cellulose. Jour. Appl. Phys. 30: 1654-1662.

DISCUSSION

Question: Was the dyeing done on dried or never-dried fibers?

Dr. Nelson: The fibers were freeze-dried upon removal from the immature cotton boll and were extracted with hot 2-aminoethanol, washed, and kept wet with water until they were put into the dyebath.

EFFECTS OF SUBSTITUENTS AND GEOMETRY OF 4,5-DIHYDROXY-2-IMIDAZOLIDINONE ON REACTIVITY AND ON HYDROLYSIS OF CELLULOSE DERIVATIVES

by
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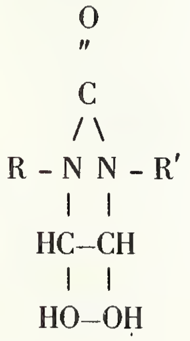
Southern Utilization Research and Development Division
(Presented by S. L. Vail)

ABSTRACT

The 4,5-dihydroxy-2-imidazolidinone system (I), regardless of the substituent in the 1,3-positions, has been known for some time to be an effective crosslinking system for cellulose. The ring hydroxyls and the pendent methylol groups are both capable of reaction under relatively mild crosslinking conditions. Although much has been written about some members of this system, the effects of geometry of the ring hydroxyls and of impurities in the system have received little attention. Some of these effects are discussed as are the properties of the finished fabrics derived from I.

INTRODUCTION

The 4,5-dihydroxy-2-imidazolidinone system (I),



I

Ia: $R=R'=CH_2OH$

Ib: $R=H,R'=CH_2OH$

Ic: $R=R'=H$

Id: $R=CH_3,R'=CH_2OH$

Ie: $R=R'=CH_3$

regardless of the substituent in the 1,3-positions, has been known for some time to be an effective crosslinking system for cellulose. The commercially important agent 4,5-dihydroxy-1,3-bis(hydromethyl)-2-imidazolidinone (Ia), and similar agents wherein the methylol groups have been replaced by hydrogen or methyl groups are members of this system.

Experimental details.—The cotton fabric used in these investigations was a desized, caustic boiled and bleached 80 x 80 white cotton printcloth weighing 3.2 to 3.4 oz./sq. yard. Fabrics were treated under conventional pad-dry-cure conditions. No softener was used. Catalysts, zinc nitrate or magnesium chloride, were added to pad baths just before padding. Catalyst percentages reported are based on solution weight.

Padding was done in the usual manner with two dips and two nips. Roll pressure was adjusted to give 70 to 80 percent wet pickup. Fabrics were then dried on pin frames at the original dimensions in an oven with circulating air at 60° to 70° C. for 7 minutes and cured at 160° for 3 minutes.

In delayed curing experiments, the dried fabrics were placed in polyethylene bags and sealed. When these bags were open to cure the fabrics, the extent of formaldehyde odor was noted before their removal from the bag.

The nuclear magnetic spectra were obtained from a Varian A60-A spectrometer equipped with a V-6040 variable-temperature probe.

Results and discussion.—In the synthesis of I, unsubstituted urea or a substituted urea must be added to glyoxal. In the cyclization step of the reaction the hydroxyls can become either cis or trans. Previous work (7) has shown that Ic occurs only as the trans isomer, whereas Ie occurs in both cis and trans forms. However, in aqueous solution cis-Ie converts rapidly to trans-Ie. The geometry of the commercially important Ia has not been reported and Id is a new compound.

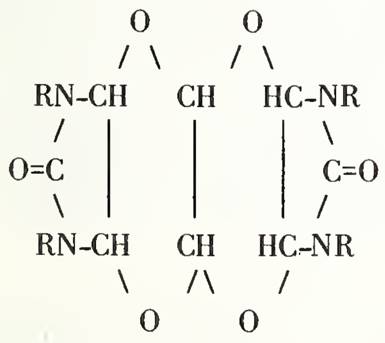
The nuclear magnetic resonance (nmr) spectra at 80° C. of a number of concentrated, commercial solutions of Ia were compared, and the main peaks were found to be identical to an authentic sample of trans-Ia prepared from trans-Ic and formaldehyde. In these spectra the ring protons are a sharp singlet, whereas the methylol ($-CH_2OH$) protons are seen as two sharp peaks. The spectra were not as clear as desired, but heating the sample to 80° appeared to move the water peak from these signals. Since the occurrence of two peaks for the methylol protons is difficult to rationalize, the trans-Ia solutions were subjected to a periodate oxidation. Unreacted glyoxal and cis-Ia are expected to be oxidized. However, since the amount of material oxidized by the periodate was very small, it was concluded that essentially no cis-Ia was present and and only glyoxal was being oxidized.

The reactivity of Ia with cotton has been found (4) to be somewhat lower than that of other N-methylolureas. It has been our experience that some batches of commercial Ia have exhibited even lower reactivity. Since the isomer is the same in all cases, it was concluded that impurities, such as sodium glycolate, might deactivate the curing catalyst. Studies have shown that from 0.1 to 0.3 percent added sodium glycolate will effectively neutralize 0.5 percent $Zn(NO_3)_2 . 6H_2O$ in an aqueous solution of commercial Ia. However, the same amount of glycolate does not effectively neutralize 4 percent $MgCl_2 . 6H_2O$ in a similar formulation.

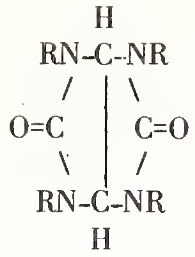
To be consistent with the above usage of the term "reactivity," we should not refer to fast-reacting or slow-reacting Ia. The active material is the same in all cases, trans-Ia; however, the catalyst systems used in curing will react differently to the acidic or basic impurities in the solution. For example, Ia prepared under alkaline conditions from a glyoxal solution which contained a high concentration of glycolic acid, would be the same cross-linking agent formed under acidic conditions, but the alkali glycolate present could neutralize the curing catalyst. On the other hand, a small amount of a hydroxy-substituted carboxylic acid, such as glycolic acid or citric acid, in the pad bath could form a highly active catalyst (5) with the conventional curing catalysts, zinc nitrate, or magnesium chloride. Thus, since glycolic acid is present in commercial glyoxal, it could well be that the strength of the acid or base used in synthesis of Ia or in subsequent steps would have a significant effect upon the strength of the curing catalyst. In a similar fashion removal of sodium ions using ion exchange should produce a more active catalyst system.

To summarize to this point, it is generally expected that all agents of type I will exist as *trans* isomers in solution with the exception of Ie. Although *cis*-Ie is isolable, it readily converts to *trans*-Ie in solution and no differences in reactivity of the isomers with cotton have been reported. Gross differences in apparent reactivity of commercial Ia are thought to be caused by the presence of impurities that affect the curing catalyst and not to the presence of isomeric materials.

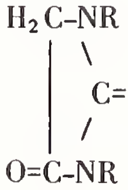
The replacement of $-CH_2OH$ in Ia with $-CH_3$ or H produced some interesting textile results. However, before considering these results, it would be well to list some of the products obtained from additions of ureas to glyoxal. Compounds of structure I, II, III, and IV are reported to form under acidic conditions (1, 3, 7), whereas I and V are reported to form under alkaline conditions (2). Under the mild acidic or basic addition conditions normally used to synthesize I, II and V are expected to be the most difficult by-products to exclude from a textile refinishing reagent. In this work only a minor contamination of V in Id is considered to be likely.



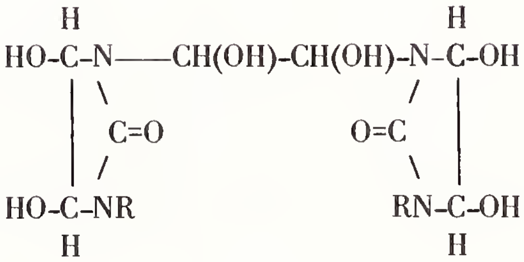
II



III

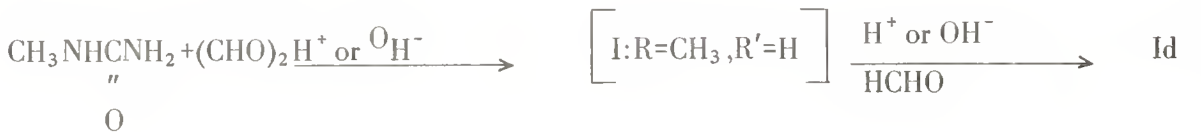


IV

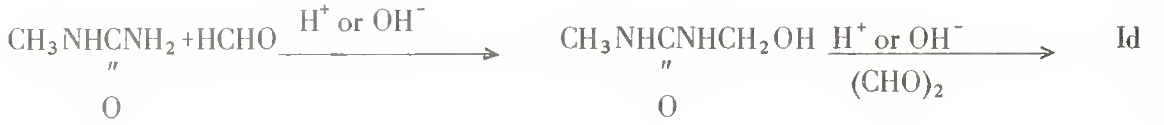


V

The isolation of a glyoxal-methylurea adduct, I: $R=CH_3$, $R'=H$, has never been reported. We have followed this addition under acidic and basic conditions using nmr and noted that several products were forming. Therefore, only crude Id was synthesized. This was attempted under acidic and basic conditions by altering the addition order of glyoxal and formaldehyde to methylurea as shown in equations 1 and 2. Adducts prepared in this manner were used to crosslink cotton. It was determined that under basic conditions the addition of methylurea to formaldehyde followed by the addition of this adduct to glyoxal consistently produced fabrics with the highest wrinkle recovery angles. This order of addition should suppress formation of V. From an nmr spectrum of crude Id it was estimated that the product was about 80 percent pure.



$$CH_3NH\underset{\underset{O}{\|}}{C}NH_2+(CHO)_2\xrightarrow{H^+\text{ or }OH^-}\left[I{:}R=CH_3,R'=H\right]\xrightarrow[HCHO]{H^+\text{ or }OH^-}Id \qquad (1)$$



$$CH_3NH\underset{\underset{O}{\|}}{C}NH_2+HCHO\xrightarrow{H^+\text{ or }OH^-}CH_3NH\underset{\underset{O}{\|}}{C}NHCH_2OH\xrightarrow[(CHO)_2]{H^+\text{ or }OH^-}Id \qquad (2)$$

In delayed curing experiments, fabrics treated with Id were found to process very well. The padded, dried fabrics used in these experiments were essentially free of formaldehyde odor during the 7-, 14-, or 21-day storage period. It is expected that in a large-scale process the formaldehyde odor would be less than that encountered in present similar processes. A delay in curing of up to 21 days did not appear to reduce the desired properties of the treated fabrics. A wrinkle recovery angle of 282° (warp plus filling) was the highest conditioned wrinkle recovery angle recorded for any treatment in these series of experiments. This recovery was obtained without the use of softeners on fabrics that had been stored for 14 days before curing.

The reduction in the amount of formaldehyde used to prepare Ia and the substitution of a methyl for a methylol reduce the functionability of the agent to two or three and also produce some interesting effects on the extent of hydrolysis of the cellulose derivatives. The reduction of the functionality has only a minor effect upon the wrinkle recovery developed, but the presence of > NH groups in the finish results in low resistance to alkaline hydrolysis. This was shown in experiments wherein fabrics were hydrolyzed for 30 minutes at 22° C. in 1N sodium hydroxide.

Based on these and other tests, Ic must be rated as being extremely susceptible to alkaline hydrolysis; possibly it is the most susceptible of known N-methylol type finishes. Similar results were obtained in multiple home launderings; however, the finish from Ib displayed less resistance to alkaline hydrolysis during laundering than shown by the aqueous sodium hydroxide.

Acidic hydrolysis of these finishes produced results that were predictable. That is, insertion of electron donating N-methyl groups reduces the resistance of the finish to hydrolysis by acid. Data of this nature are shown in experiments, wherein fabrics were treated for 30 minutes at 40° C. with 0.1N hydrochloric acid. Based on the reactivity-hydrolysis rate relationship (6), a general order of reactivity of DMEU = Ie > Id > Ia is suggested.

Fabrics finished with I in a conventional manner generally display similar strength and abrasion properties. All are susceptible to discoloration during curing, particularly with delayed cures. Recently it has been noticed that several commercial firms produce solutions of Ia that do not usually discolor fabrics on curing. However, color is often developed from these solutions of Ia if they are stored for too long a period before use. Within limits, the amount of unreacted glyoxal in solution does not relate directly to amount of discoloration. However, less than two moles of formaldehyde added to Ic appears to increase the intensity of discoloration. Regardless of how pure it may be, Ic discolors fabric badly on curing.

No attempt was made to quantitatively estimate the amount of formaldehyde released by I during a delayed cure. All of these agents release little or no formaldehyde. Obviously, Ic and Ie cannot release formaldehyde, whereas, Ib and Id are capable of releasing only one mole. Indeed, in a qualitative sense, Ib and Id are almost odorless in laboratory tests. All finishes except those obtained from Id and Ie are susceptible to chlorine damage in the scorch test.

REFERENCES

1. Barker, R. H., Vail, S. L., and Barcelo, G. B. 1966. Tetracyclic Acetal from N,N'-Dimethylurea and Glyoxal. Jour. Heterocyclic Chem. 3: 354.

2. Dinwoodie, A. H., Fort, G., and Thompson, J. M. C. 1967. Base-Catalysed Reactions of Glyoxal. Part III. 1,2-Bis-(2-Oxoimidazolidin-1-yl)ethan-1,2-Diols. Jour. Chem. Soc. (C): 2565-2568, and references herein.

3. Nematollahi, J., and Ketcham, R. 1963. Imidaziomidazoles. I. The Reaction of Ureas with Glyoxal. Tetrahydroimidazo[4,5-d] imidazole-2,5-Diones. Jour. Org. Chem. 28: 2378-2380.

4. Petersen, H. 1968. Reaction Mechanisms, Structure, and Properties of Methylol Compounds in Cross-Linking Cotton. Textile Res. Jour. 38: 156-176.

5. Pierce, A. G., Jr., and Frick, J. G., Jr. 1968. Highly Active Catalysts for Wrinkle Resistance and Wash-Wear Finishing of Cotton Fabric. Amer. Dyestuff Reptr. 57: P864-P868.

6. Vail, S. L. 1967. New Crosslinking Agents for Cellulose and Their Uses in Post Curing. Chem. & Indus. 305-309.

7. Vail, S. L., Barker, R. H., and Mennitt, P. G. 1965. Formation and Identification of cis- and trans- Dihydroxyimidazolidinones from Ureas and Glyoxal. Jour. Org. Chem. 30: 2179-2182.

THIRD SESSION: P. J. Fynn, J. C. Penney Co., Inc., New York, N. Y., Chairman

RECENT DEVELOPMENTS IN THE CHEMISTRY OF CELLULOSE WHICH PERTAIN TO THE CROSS-LINKING OF COTTON

by
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Southern Utilization Research and Development Division
(Presented by S. P. Rowland)

ABSTRACT

The distributions of sites of attachment of substituents or cross-linkages (a) at the 2-0-, 3-0-, and 6-0-positions of the D-glucopyranosyl units, (b) along the molecular chains of cellulose, (c) on or in the microstructural units, and (d) within the fiber cross sections are reviewed in order to develop perspective for the factors that influence and control these distributions.

Among the factors determining the site of attachment in the D-glucopyranosyl unit are: (1) The type of reaction (e. g., reversible or nonreversible), (2) the specific nature of the reagent, for example, molecular size, and (3) the medium from which the reagent is introduced. Means of controlling this distribution are discussed.

There is no available information on the distributions of linkages introduced along the molecular chains of cellulose from reactions that occur without disruption of the crystalline order. It is evident, however, that even under these conditions, every molecule in the cellulose matrix has one or more accessible segments along its chain. Measurements specific to the distribution of substituents among the total D-glucopyranosyl units, but applicable in first order approximation to the units along the molecular chain, are discussed in connection with reactions conducted in mercerizing media.

Evidence indicative of reactions occurring on the surfaces of highly ordered microstructural units (microfibrils or bundles of microfibrils) has been obtained from measurement of the distribution of substituents introduced into the D-glucopyranosyl units of cotton cellulose under nonmercerizing conditions. Penetration within these units is evident under mercerizing conditions of reaction. An interrelationship between the site of attachment in the D-glucopyranosyl unit and the site of reaction in the microstructural unit is discussed.

At the fiber level of structure, the complex interplay between rate of chemical reaction and rate of diffusion into the fibers is considered. Gross variations of distribution of substituents or cross-linkages in the fiber cross section (from peri-

pheral to uniform) result from changes in the two rates noted. In a case examined in some detail, wrinkle-recovery angles benefit from the more uniform distribution of cross-linkages.

INTRODUCTION

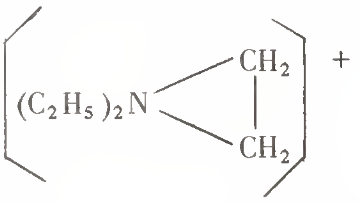
While there is considerable technical and commercial interest in the chemical modification of cotton cellulose in the fabric form to develop easy-care and permanent-press performance properties, the details of the chemistry of the reactions of fibrous cellulose remain rather obscure. Within the last 2 years and since a preceding report (25), substantial progress has been made in clarifying certain aspects of the chemistry of the reactions of cotton cellulose. The object of this review is to bring this information together so that a degree of perspective may be developed toward the broad picture. This information provides a basis for a better understanding of the complexities involved in the cross-linking of cotton cellulose; it may serve also as a basis for new or modified ways of controlling the chemistry of cellulose and of developing superior performance characteristics in the modified fabrics. Lastly, this selected review serves to accentuate those areas where further studies are especially desirable.

DISCUSSION

Distribution of substituents or linkages on the D-glucopyranosyl units of cotton cellulose.—Most of the information that is available on the distribution of substituents in the D-glucopyranosyl units of cotton cellulose is from data on nonreversible Williamson etherification reactions (table 1).

In these reactions, which have been conducted in sodium hydroxide solutions of mercerizing strength, there is a distinct trend of decreasing substitution in the 2-0-position (relative to that in the 6-0-position) as the size of the substituent group increases; for example, reactions of methyl chloride, ethyl chloride, and sodium chloroacetate. This ratio of substitution at the 2-0-position to substitution at the 6-0-position also decreases as the size of the total reagent molecule increases, that is, methyl chloride vs. dimethyl sulfate. Substitution at the 3-0-position follows a similar, but less pronounced, trend.

A striking example of the possible effect of reaction mechanism on the distribution of substituents lies in the reactions of 2-(diethylamino)ethyl chloride and sodium 2-aminoethyl sulfate. The larger 2-(diethylamino)ethyl group is introduced into the 2-0-position more readily than the smaller 2-aminoethyl group. The reaction of sodium 2-aminoethyl sulfate appears to occur by displacement of the sulfato unit from $H_2NCH_2-CH_2OSO_3$ with the approach of the cellulosate ion (24). On the other hand, the 2-(diethylamino)ethyl chloride reacts, following the dissociation of the chloride ion, through the diethylaziridinium ion,



, which is much less sterically hindered (19,23).

Table 1.–Distribution of substituents in the D-glucopyranosyl units of cotton cellulose resulting from irreversible reactions carried to low degree of substitution

Reagent	Reaction medium	Distribution of substituents[1]				Reference
		2-0-	3-0-	6-0-	DS	
Methyl chloride	18.9 percent NaOH	2.79	0.46	1.00	0.82	4
Ethyl chloride	16.4 percent NaOH	2.39	0.46	1.00	0.76	5
Dimethyl sulfate	Homogeneous[2]	1.85	0.40	1.00	0.59	7
	18.9 NaOH	1.85	0.45	1.00	0.28	7
	35 percent NaOH	1.83	0.40	1.00	0.63	7
2-(Diethylamino) ethyl chloride	20 percent NaOH	1.27	0.35	1.00	0.05	23
Sodium chloroacetate	ca. 44 percent NaOH	0.75	0.34	1.00	0.09-2.0	8
Sodium allyl sulfate	20.7 percent NaOH	0.7	0.2	1.00	0.07	16
Sodium 2-aminoethyl sulfate	24 percent NaOH	0.60	0.14	1.00	0.14	24
Ethylene oxide	18.9 percent NaOH	0.30	0.09	1.00	0.60[3]	6

[1] These numbers express the ratios of substituents present in the monosubstituted glucose fraction as a result of chemical modification of cellulose to the DS indicated. Distributions were obtained from hydrolysis of the chemically modified celluloses to glucose and substituted glucoses, followed by gradient elution chromatography or gas-liquid chromatography.

[2] Dissolved in benzyltriethylammonium hydroxide.

[3] Molar substitution.

The greater stearic effect and, therefore, the lower proportion of reaction at the 2-0-position would be expected for the reaction involving sodium 2-aminoethyl sulfate.

The distribution of 2-hydroxyethyl substituents in the products of the reaction of ethylene oxide with cellulose shows a pronounced preference for reaction at the 6-0-position. This is hardly surprising since etherification by ring-opening of an epoxide is quite different from etherification by displacement of a halogen or sulfato group. The low proportion of reaction at the 2-0-position may be because of a highly selective approach which is required between the cellulosate ion and the ethylene oxide molecule.

Relative to the development of unique performance properties in the chemically-modified cotton celluloses, it is important to know whether it is possible to obtain different distributions of substituents with a specific reagent. Preliminary information, when the reagent involved is 2-(diethylamino)ethyl chloride (22), is in table 2. The reaction conducted in nonaqueous medium results in a substantially greater proportion of substitution at the 2-0- and 3-0-positions. The change in the distribution of substituents in the D-glucopyranosyl units of starch (whose units are joined by α-linkages in contrast to the β-linkages in cellulose) with change in conditions of reaction is generally similar. The magnitude of the responses of cellulose and of starch to the change in reaction conditions is impressive in view of the lack of change in the distribution of methyl groups resulting from methylation reactions with dimethyl sulfate in the various media noted in table 1. An explanation for the change in the distribution of substituents as a consequence of reaction in nonaqueous media will be presented in a later section.

The reversible reactions of the hydroxyl groups of cellulose are even more pertinent to our interest in the cross-linking of cotton cellulose. The most interesting reagents that undergo reversible reactions with hydroxyl groups are activated vinyl compounds, carboxylic acids, N-methylol compounds, and formaldehyde. Distributions of substituents in products from reversible reactions involving these reagents (table 3) are particularly interesting in those cases where it has been possible to measure the extent of reaction at each specific hydroxyl group. It is evident that acrylamide, methyl vinyl sulfone and formaldehyde are all characterized by relatively high reactivity at the 6-0-position and by very little reactivity at the 3-0-position.

In none of the publications listed in table 3 has the state of equilibrium in the product been described. Recently, equilibrium has been considered in some detail (26). The effect of state of equilibrium upon the distribution of substituent groups is shown in table 4. Each of these reactions involved padding of the cotton fabric in a 20-percent solution of methyl vinyl sulfone followed by padding in a 10-percent solution of sodium hydroxide saturated with sodium sulfate (26). The relative substitution in the 2-0-position decreased with increasing opportunity for

Table 2.—Effect of conditions of reaction on the distribution of 2-(diethylamino)ethyl substituents (22)

Substrate	Reaction	Distribution of substituents [1]			
		DS	2-0-	3-0-	6-0-
Cotton linters	20 percent NaOH; aqueous DEAE Cl, [2] 85°, 50 min.	0.64	1.25	0.35	1.00
Cotton fabric	20 percent aqueous DEAE Cl; 20 percent NaOH [3] 25°, 19 hr.	0.048	1.27	0.35	1.00
Cotton fabric	DEAE Cl and KOH in dioxane, 100°, 3 hr.	0.026	2.50	0.50	1.00
Corn starch	20 percent aqueous DEAE Cl; 20 percent NaOH, 25°, 19 hr.	0.083	1.08	0.45	1.00
Corn starch	DEAE Cl and KOH in dioxane, 100°, 3 hr.	0.024	3.00	1.50	1.00

[1] In the monosubstituted glucose fraction.

[2] DEAE Cl designates the reagent, 2-(diethylamino)ethyl chloride, in the form of its hydrochloride.

[3] Saturated with sodium sulfate.

Table 3.—Distribution of linkages in the D-glucopyranosyl units of cotton cellulose resulting from reversible reactions[1]

Reagent	Reaction	Distribution of substituents				Reference
		2-O-	3-O-	6-O-	DS	
Acrylamide	ca. 20 percent NaOH; acrylamide, 4°, 73 hr.	0.47	0.05	1.0[2]	0.78	34
Acrylonitrile[3]	Aqueous acrylonitrile and NaOH, 30° 2 hr.	(ca. 1.3)		1.0[2,4]	0.24	20
Methyl vinyl sulfone	20 percent methyl vinyl sulfone; 10 percent NaOH, 25°, 1 hr.	0.20	0.03	1.0[5]	0.11	26
Acetic acid[6]	$(CH_3CO)_2O$ and CH_3COOH, H_2SO_4, 60°, 2-5 hr.	(ca. 1.1)		1.0[2,4]	0.52	9
Formic acid[6]	60.7 percent, HCOOH, 38.8 percent H_3PO_4, 0.5 percent, P_2O_5, 20°, 2 hr.	(ca. 1.2)		1.0[2,4]	0.40	9
Methylolmelamine	Resin "wet cure process"	(0.64)		1.0[2,7]	0.04	36
Trimethylolmelamine	Pad in aqueous reagent, cure at 160°, 2 min.	(1.18)		1.0[2,7]	0.16	36
Methylated trimethylolmelamine	Pad in aqueous reagent, cure at 160°, 2 min.	(2.31)		1.0[2,7]	0.30	36
Formaldehyde	HCl; CH_2O Vapors 95° C, 7-12 hr.	0.33	0.05	1.0[8]	0.43[9]	1
	Paraformaldehyde and conc. hydrochloric acid in DMSO[10] 90°, 5 hr.	0.32	0.14	1.0[8]	0.07[9]	21

Table 3.–Distribution of linkages in the D-glucopyranosyl units of cotton cellulose resulting from reversible reactions 1/–continued

Reagent	Reaction	Distribution of substituents				Reference
		2-0-	3-0-	6-0-	DS	
Formaldehyde (cont'd.)	Aqueous formalin and conc. hydrochloric acid 20°, 30 min.	0.38	0.10	1.0 8/	0.07 9/	21
	Acid, 20°, 30 min. CH_2O-HCl vapors, 110°, 1 hr.	0.31	0.18	1.0 8/	0.29 9/	21

1/ Cotton cellulose was the substrate for reactions except as noted. In certain cases the distributions of substituents in the 2-0- and 3-0-positions were not determined separately. The estimate of the combined substitution at the 2-0- and 3-0-positions is indicated in these cases by a single number in parentheses.

2/ Substituents in mono-, di-, and trisubstituted D-glucopyranosyl units were considered.

3/ Wood pulp.

4/ Measured indirectly by methods such as tritylation and tosylation.

5/ Direct isolation and identification of monosubstituted D-glucopyranosyl units in gas-liquid chromatography.

6/ Regenerated cellulose.

7/ Extensive series of reactions to introduce methyl groups at the site formerly occupied by resin linkages to the D-glucopyranosyl units.

8/ Chromatographic isolation and identification of D-glucopyranosyl units containing methyl groups at all positions not formerly occupied by the formaldehyde linkage. Only the ratio of the di-3,6-0-, di-2,6-0-, and di-2,3-0-methyl-D-glycopyranoses (corresponding to the monosubstituted fraction) is considered here.

9/ This is the apparent DS for the formaldehyde in mono-oxymethylene cross-linkages.

10/ DMSO is dimethyl sulfoxide.

Table 4.—Effect of state of equilibrium in the reaction of methyl vinyl sulfone with cotton cellulose upon the distribution of O-(methylsulfonylethyl) substituents in the D-glucopyranosyl units (26)

Process 1/	Cure 2/	Distribution of substituents 2-0-	3-0-	6-0-	DS
Rapid	140°, 5 min	0.75	0.00	1.00	0.08
Normal laboratory operation	140°, 5 min	0.28	0.10	1.00	0.14
Normal laboratory operation	25°, 1 hr (in polyethylene bag)	0.22	0.05	1.00	0.11
Normal laboratory operation	25°, 24 hr (in polyethylene bag)	0.14	0.05	1.00	0.09

1/ Cotton print cloth padded in a 20-percent aqueous solution of methyl vinyl sulfone to a 100-percent wet pickup and then in a 10-percent solution of sodium hydroxide saturated with sodium sulfate to an additional 50-percent wet pickup. Entries in this column refer to the speed of the processing operations between the time of entry of the fabric into the caustic solution and the time of insertion of the fabric into the curing chamber.

2/ Evidently reaction or "cure" actually starts at room temperature as soon as the cellulose-methyl vinyl sulfone is contacted with the strong base.

the reaction to approach equilibrium. Thus, it is reasonable to conclude that the relatively low substitution at the 2-0-positions in the reversible reactions listed in table 3 constitutes evidence that the products of these particular reactions were approaching a state of equilibrium. Most likely, as is exemplified by the data for methyl vinyl sulfone, each of the reactions in table 3 has been arrested short of true equilibrium. In the methyl vinyl sulfone-cellulose reaction, attainment of equilibrium appears to be almost complete with a distribution of substituents at the 2-0-, 3-0-, and 6-0-positions in the ratio of 0.14: 0.05: 1.00. The first approximation, very similar ratios may be expected to develop at equilibrium in the products from other reversible reactions. It is evident from the foregoing data that an equilibrium-controlled distribution of substituents is approached in "wet cure" reactions (third and fourth entries in table 4) whereas in the "bake-cure" process (first entry in table 4) a rate-controlled distribution of substituents is approached.

Distribution of substituents or linkages along the molecular chains of cellulose.—An uneven distribution of substituents along the molecular chains of methyl celluloses having degrees of substitution substantially greater than one is shown by the results of enzymatic hydrolysis that occurs only at sites of unsubstituted D-glucopyranosyl units (11, 31). However, quantitative methods for measuring the degree of uniformity of distribution of substituents among the D-glucopyranosyl units along the molecular chain remain to be developed. Some pertinent information is available from indirect measurements and is discussed in the following paragraphs.

The fibrous and crystalline natures of cotton cellulose generally preclude accessibility of reagents to all of the D-glucopyranosyl units along the molecular chains. Even in mercerizing media, in which swelling occurs and the lateral interrelationships between D-glucopyranosyl units are changed, the randomness of reaction with the D-glucopyranosyl units is less than that which characterizes a homogeneous reaction of cellulose. This is illustrated in figure 1 with data of Croon and others (3,4,5,6,7,8) and Cirino and others (2). The decrease in the fraction of unsubstituted D-glucopyranosyl units (S_0) is treated as a function of the extent of reaction. The curves represent the calculated values for homogeneous reactions in which the individual hydroxyl groups have rate constants in the ratio 1:1:1 and 0.1:0.1:1 (32). The deviation from random reaction among the D-glucopyranosyl units is illustrated in a general way by the location of experimental data above selected calculated curves. Increasing deviation from random reaction is shown in the series (a) dimethyl sulfate with cellulose dissolved in a quaternary ammonium hydroxide, dimethyl sulfate with cellulose in 18.9 percent sodium hydroxide, and dimethyl sulfate with cellulose in 35 percent sodium hydroxide; and (b) methyl chloride, ethyl chloride, and dimethyl sulfate with cellulose in 16.4 or 18.9 percent sodium hydroxide. Aside from the homogeneous reaction, the most random reaction resulted with the smallest reagent molecule (methyl chloride) and in the mercerizing medium of lower concentration of sodium hydroxide. The size of the reagent molecule undoubtedly imposes a limitation upon larger reagent molecules in penetrating with the mercerizing agents into formerly crystalline regions of the cellulose matrix. Decreasing randomness of reaction with increasing concentration of the mercerizing medium is probably an indication of decreased solubility of reagent in the more concentrated caustic solution.

A random reaction among the D-glucopyranosyl units of cotton cellulose is assumed by Touzinsky (34) for the reaction of acrylamide in mercerizing media. However, a significantly nonrandom reaction was observed by Cirino and others (2) in the case of the reaction of methyl vinyl sulfone with cotton cellulose under similar conditions (compare plus designations in fig. 1 with the lower theoretical curve). Thus, mercerizing conditions, even with long equilibration periods,

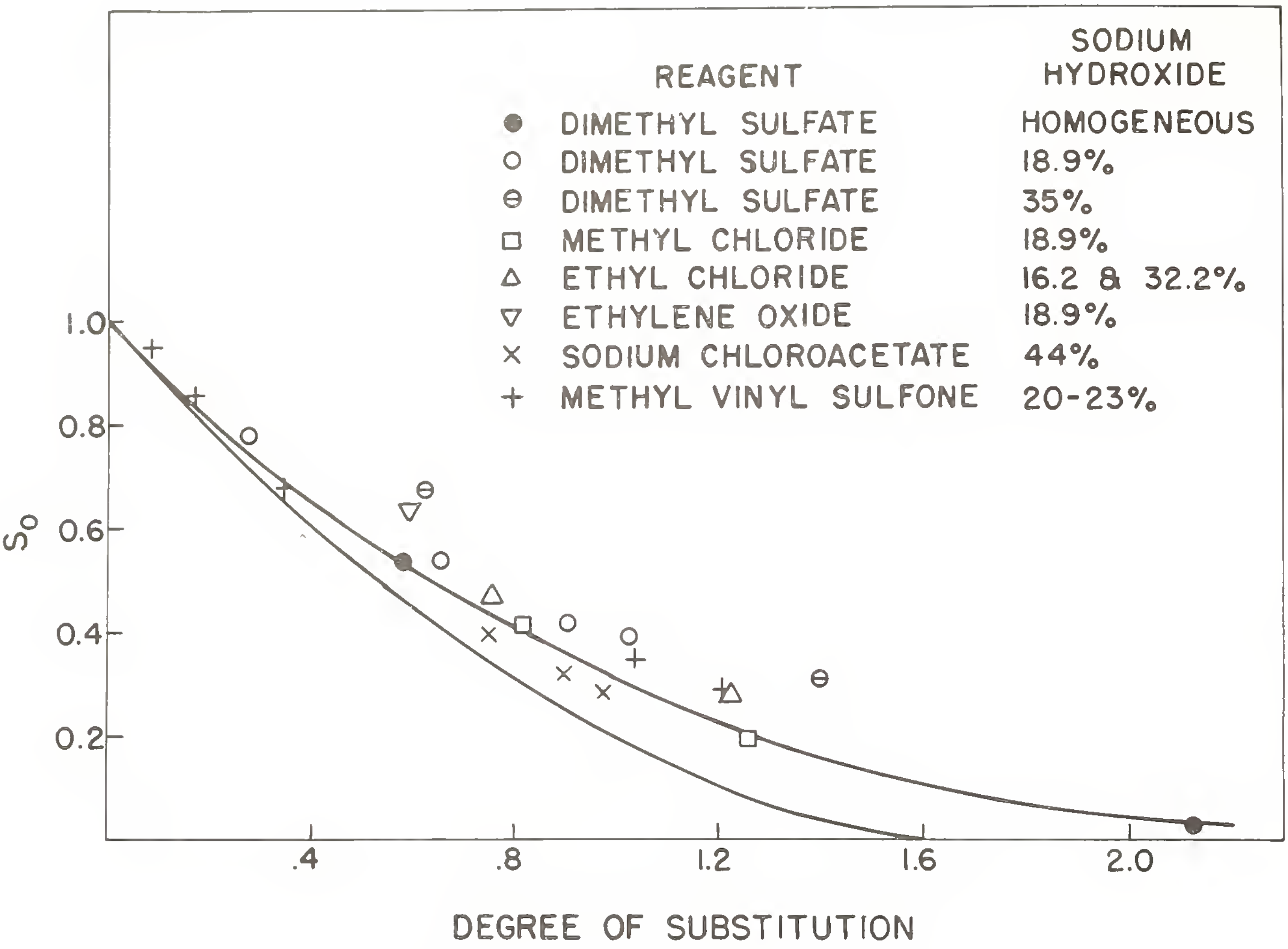


Figure 1.–Mole fraction of unsubstituted D-glucopyranosyl units (S_0) as a function of the degree of substitution for a variety of reactions. The curves represent the theoretical values calculated for homogeneous reactions in which the hydroxyl groups have relative rate constants in the ratio of 1:1:1 (upper curve) and 0.1:0.1:1.0 (lower curve).

are insufficient to achieve random reaction among all of the D-glucopyranosyl units.

There is considerable evidence that the presence of a substituent at the 2-0-position increases the reactivity of the hydroxyl group at C-3 (2,3,5,6,7,8). The result is a higher degree of polysubstitution in the D-glucopyranosyl units than expected on the basis of the relative reactivities of the individual hydroxyl groups in the unsubstituted D-glucopyranosyl units (4). The degree of activation of the hydroxyl groups at C-3 is readily apparent from the ratio of 3-0- to 6-0-substitution in the polysubstituted D-glucopyranosyl units as compared to the same ratio for the monosubstituted units. This ratio in the polysubstituted fractions of chemically modified cotton celluloses is 1.3 to 4.5 times that in the monosubstituted fractions (table 5). Only in the case of the reaction of sodium chloroacetate with cellulose is there no increase in this ratio in the polysubstituted fraction. Here it appears that a "normal" activation of the hydroxyl

Table 5.–Activation of the hydroxyl group at C-3 by substitution at the 2-0-position

Reagent	Reaction medium	DS	Distribution of substituents at the 3-0-position 1/		Reactivity factor 2/	Reference
			Monosubstituted glucose fraction	Polysubstituted glucose fraction		
Methyl chloride	18.9 percent NaOH	0.82	0.46	0.72	1.57	4
Ethyl chloride	16.4 percent NaOH	0.76	0.46	0.75	1.63	5
Dimethyl sulfate	Homo-geneous	0.59	0.40	0.94	2.35	7
Sodium chloro-acetate	44 percent NaOH	0.75	0.40	0.39	0.98	8
Ethylene oxide	18.9 percent NaOH	0.60 3/	0.094	0.42	4.47	6

1/ Ratio of 3-0- to 6-0-substitution.

2/ The ratio of 3-0- to 6-0-substitution in the polysubstituted glucose fraction divided by the corresponding ratio in the monosubstituted glucose fraction.

3/ Molar substitution.

group at C-3 by the presence of a substituent in the 2-0-position is counterbalanced by an electrostatic contribution of ionic substituent (—CH_2COO^-). This substituent may repress development of the cellulosate ion at C-3 or the approach of another molecule of reagent or both. In any case, the result is to increase the probability that the next molecule of reagent will react at another D-glucopyranosyl unit rather than at one that is already partly substituted. Such an explanation accounts for the unique randomness of distribution of carboxymethyl substituents in carboxymethyl cellulose (see fig. 1). It should be noted that the foregoing data and explanation apply to base-catalyzed reactions which proceed through cellulosate ions and that corresponding data are not available on the products from acid-catalyzed reactions.

For reactions of cotton cellulose conducted in media that are less swelling than mercerizing media, the question of distribution of substituents along the molecular chain remains completely without answer. A related question pertains to the extent to which all of the molecules of cellulose are involved in a reaction. This is most important in connection with cross-linking reactions. In certain aqueous and vapor phase systems of reaction of formaldehyde with cotton cellulose, essentially all of the molecules of the fibrous, crystalline substrate are cross-linked into the network structure at very low levels of reaction (0.01 moles of formaldehyde per D-glucopyranosyl unit) (29). These reactions occur without significant change in the crystalline structure as measured by X-ray crystallinity index. The indication is that a segment, or segments, of the chain of each molecule of cellulose is readily accessible to the reagent without disruption of the crystalline regions. The inference is that each molecule of cotton cellulose has segments of its chain that pass through noncrystalline regions or that lie on the surfaces of crystalline regions.

Distribution of Substituents or Linkages in the Microfibrillar Structure of Cotton Cellulose.—For a chemical reaction to occur between the hydroxyl groups of D-glucopyranosyl units of cellulose and a molecule of reagent, the former must be accessible to the latter. According to the fringed micelle theory of the microstructure of cellulose, molecules extend through several crystalline and disordered regions (15, pp. 216-220). Accessible hydroxyl groups are mainly those of the D-glucopyranosyl units in the disordered regions together with those lying on the surfaces of crystalline regions. In the regions of disorder, it is expected that the three different hydroxyl groups of the D-glucopyranosyl units are equally available for reactions.

In the fringed fibril theory of the microstructure of cellulose, continuous regions of crystallinity are postulated (15, pp. 221-222). The accessible hydroxyl groups are chiefly those in the D-glucopyranosyl units that lie on the surfaces of the crystalline regions, plus some hydroxyl groups in D-glucopyranosyl units in regions of imperfect order. In this case, the high degree of order which characterizes the crystalline material may be reflected in the specific hydroxyl groups which are available for reactions on the surfaces of the crystalline regions. Thus, accessibility might be expected to be different for each type of hydroxyl group.

Recently, Haworth and others (14) interpreted certain chemical data as evidence that methylation occurs on the surfaces of the elementary fibril that is observed in electron microscopy. They methylated cotton fabric repeatedly with dimethyl sulfate in 2 N sodium hydroxide; a rapid reaction was accompanied by a slower reaction. The extent of reaction and the distribution of methyl groups in the D-glucopyranosyl units were followed at each step. The rapid stage was interpreted as the methylation of hydroxyl groups on surfaces and the slower stage as the gradual penetration into the interior of microstructural units. At a point estimated to correspond to the end of the rapid stage of reaction (a DS of 0.65), 56 percent of the D-glucopyranosyl units contained no methyl substituents, that is, had no accessible hydroxyl groups. Of the remaining D-glucopyranosyl units, 89 percent had reacted to form essentially equimolar amounts of 2-0-, 6-0-, 2,6-0, and 2,3,6-0 substituted units. (The distribution of substituents in the 2-0-, 3-0-, and 6-0-positions at this point was 1.04:0.43:1.00 respectively.) This degree of inaccessibility of D-glucopyranosyl units was considered by Haworth and others (14) and later by Jeffries and others (17) to be consistent with reaction occurring on surfaces of ordered chains of cellulose having a cross section of 8 D-glucopyranosyl units on one side and 12 units on another (approximately 50 A. by 65-100 A.). Similar repeated methylations of cotton cellulose with diazomethane in ether saturated with water resulted, at the end of the rapid stage (DS = ca. 0.39), in a distribution of methyl groups that was consistent with a reaction occurring on the exterior surfaces of a bundle of four of the elementary fibrils noted above.

The foregoing data and interpretation lead to a consideration of the cotton fiber as a composite of crystalline microfibrils and a new question is posed: "Is the distribution of substituents at low DS, (in the range of 0.05-0.30, which probably characterizes conventional cross-linked cotton celluloses), a reflection of the specific accessibilities of the individual types of hydroxyl groups on microfibrilar surfaces"? Wade and others (35) examined the reaction of 2-(diethylamino)-ethyl chloride with cotton cellulose in the presence of 1 N, 2 N, and 4 N sodium hydroxide. Decreasing specificity of reaction at the 2-0-position was observed with increasing concentration of the base (fig. 2). The specificity of the reaction at the 2-0-position decreases as the swelling strength of the medium for cellulose increases.

It is now evident that the high specificity of substitution of 2-(diethylamino)-ethyl groups at the 2-0-position as the result of reaction in a dioxane medium (table 2) may be the consequence of a reaction in a medium which has little swelling action on the cotton cellulose. Thus, current evidence strongly suggests (a) that reactions of cotton cellulose in nonswelling media occur selectively on surfaces of microstructural units, (b) that

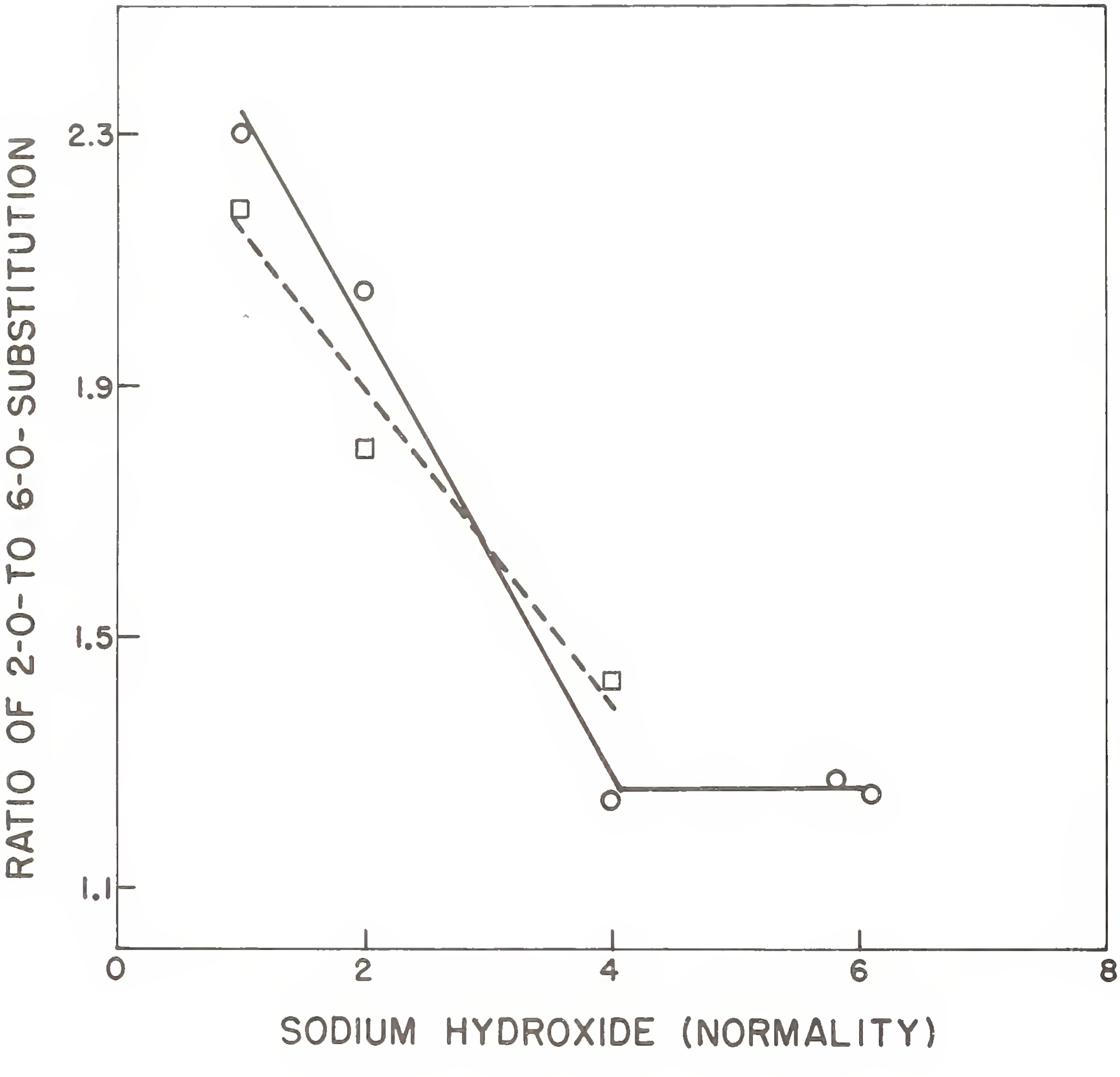


Figure 2.—Ratio of 2-0- to 6-0-substitution resulting from reactions conducted with sodium hydroxide of various normalities. The reactions involved 2-(diethylamino)ethyl chloride dissolved in water (o) and in dimethyl sulfoxide (□).

there is an increasing penetration of the reagent into the microstructural units as the swelling power of the reaction medium increases, and (c) that there is a specificity of accessibility of individual types of hydroxyl groups which is dependent, in part, upon the swelling power of the medium.

Distribution of Cross-Linkages within the Cross Section of the Cotton Fiber.—The occurrence of chemical reactions on the surface of the cotton fiber or in and throughout the fiber cross section as a function of the reagent, the medium, and other variables has been generally appreciated in cases in which the differences are pronounced (10,27,33). Recently, Gogek and Valko (12) and Willard and others (37) prepared and characterized cotton fabrics with pronounced cross-link development in the core of the fibers, on the one hand, and in the peripheral regions, on the other hand. Cross-linked compositions in which the differences are less pronounced have come to light as a result of electron micrographic analysis together with sol-gel analysis (29). However, subtle variations in the density of cross-linkages throughout the fiber cross section are difficult to assess; for this reason, the significance of this variable in the finishing of cotton fabrics may be underestimated.

The development of high wrinkle recovery angles in cross-linked cotton cellulose at very low levels of bound formaldehyde, introduced by the slow vapor-phase reaction at room temperature (13), has been attributed, at least in part, to the high degree of uniformity of the distribution of these cross-linkages throughout the fiber structure (28,29,30). The variation in the distribution of cross-linkages in the fiber structure from one that is primarily peripheral to one that is more uniform and the attendant changes in performance properties of the fabric have been characterized in a recent study (18). Dry cotton fabric was reacted with vapors of formaldehyde at 125° C. in the presence and absence of boric acid catalyst. The rates of these reactions are illustrated in figure 3. The reaction was substantially more rapid when conducted in the presence of the catalyst. At approximately the 0.15-percent level of bound formaldehyde (ca. 0.008 moles/A-GU) in these compositions, it was possible to observe, by electron microscopy of fiber cross sections, a preferential buildup of cross-linkages in the peripheral regions of the fibers from the catalyzed reaction. The distribution of cross-linkages in fibers from the uncatalyzed reaction was more uniform. At higher levels of formaldehyde in the fabrics, differences in electron micrographs of expanded cross sections were not apparent. It was evident, however, from quantitative measurements of the fraction which was insoluble in cupriethylenediamine hydroxide (gel) that the product from the catalyzed reaction was characterized by lower network development throughout the course of the reaction (fig. 4). The difference between the two compositions is the extent of cross-linking in the interior regions of the fibers and this difference persists even after several hours of reaction time.

The increases in conditioned and wet wrinkle recovery angles per unit of bound formaldehyde were greater for the

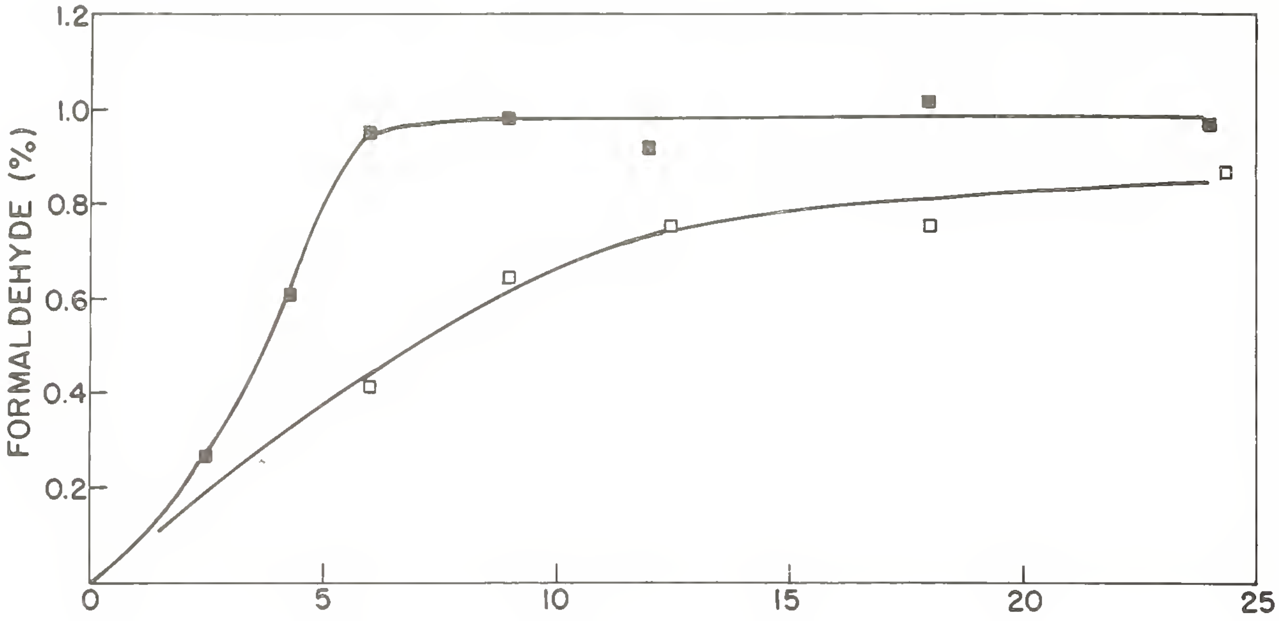


Figure 3.—Bound formaldehyde introduced into cotton fabric during various periods of reaction of formaldehyde vapors at 125° C. in the absence of catalyst (□) and in the presence of boric acid (■).

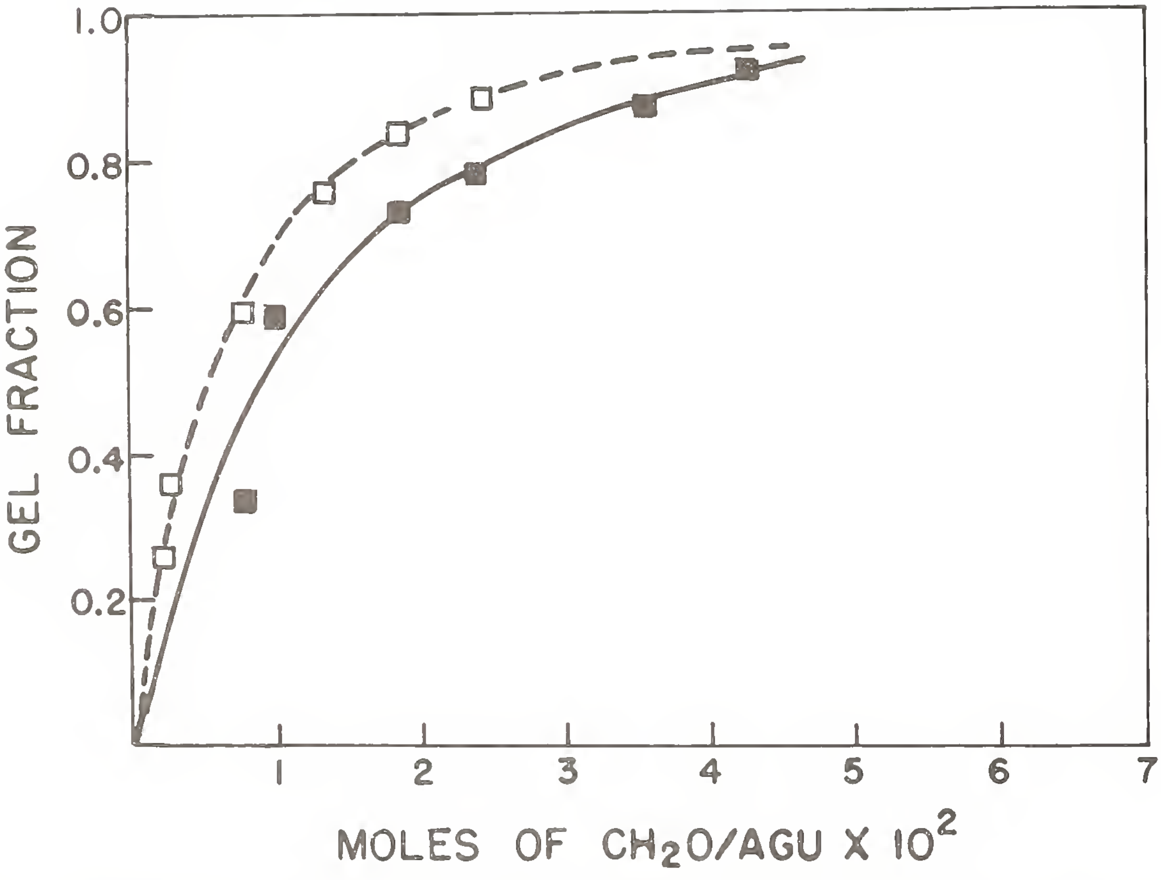


Figure 4.—Gel fraction versus moles of formaldehyde per D-glucopyranosyl unit (AGU) for cotton cross-linked with formaldehyde in the absence (□) and in the presence of (■) of catalyst.

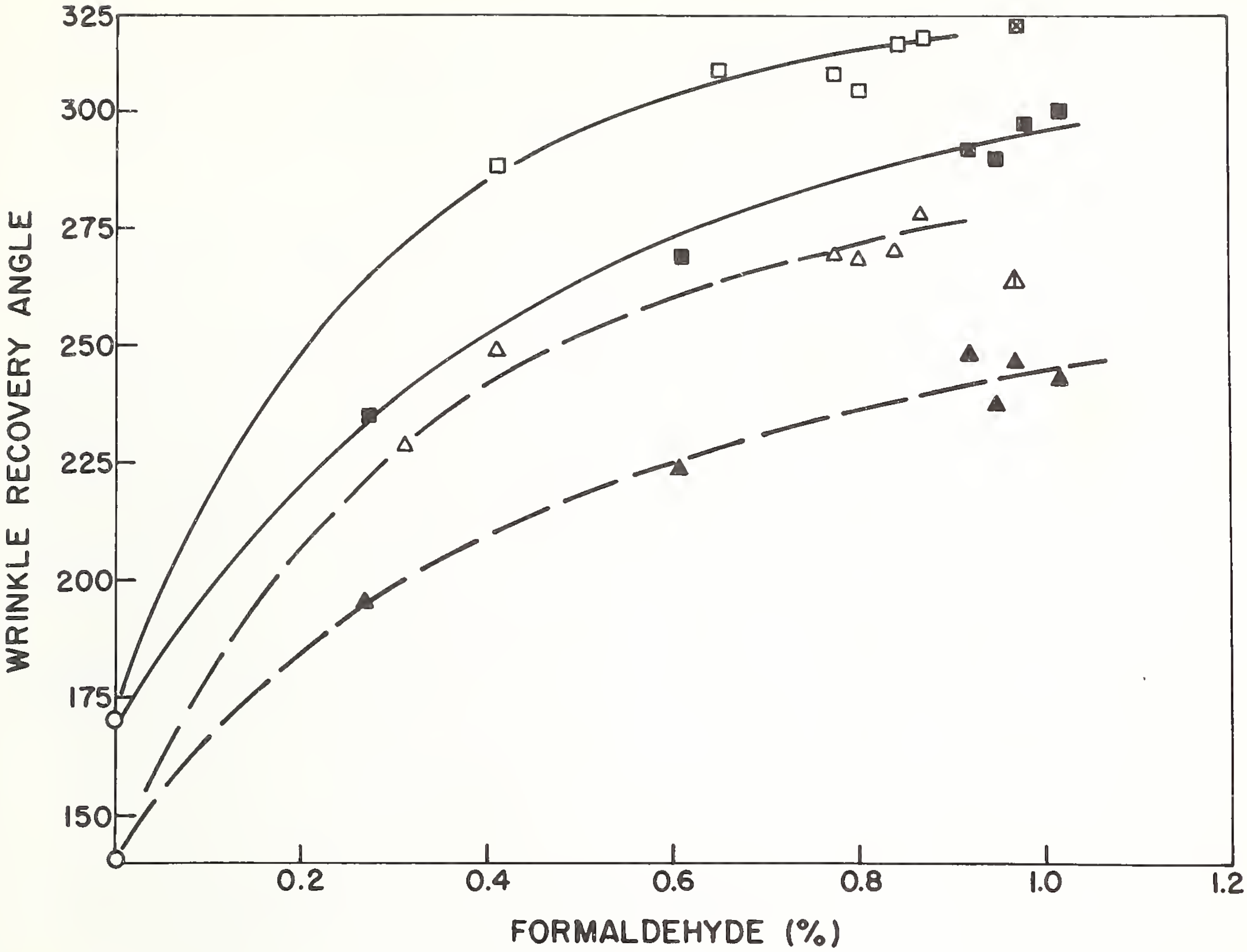


Figure 5.—Conditioned wrinkle-recovery angles (squares) and wet wrinkle recovery angles (triangles) for cotton fabric cross-linked with formaldehyde vapors in the absence (open symbols) and the presence (solid symbols) of catalyst.

cotton fabric with the more uniformly distributed cross links (fig. 5), which developed in the slower (uncatalyzed) reaction. After a 24-hour reaction period, the wrinkle recovery angles of the product from the catalyzed reaction approached those of the product from the uncatalyzed reaction (see special designations in fig. 4).

The foregoing results indicate development of higher wrinkle recovery angles for products having the more uniform distribution of cross-linkages. The more uniform distribution of cross-linkages is realized when the rate of the chemical reaction is slower than the rate of diffusion of reagent into and throughout the cotton fiber. In retrospect, it appears that there are numerous recorded instances of cross-linking reactions (18) where the higher wrinkle-recovery angles per unit of reagent develop as a result of a modification that slows the rate of the chemical reaction relative to the rate of the diffusion. The inference is that in all of these cases the higher wrinkle recovery angles are the consequence of the more uniform distribution of cross-linkages throughout the fiber.

CONCLUDING CONSIDERATIONS

Evidence from selected studies of the chemical reactions of cotton celluloses has been reviewed for the purpose of developing a perspective toward the total problem—that is of understanding and controlling the chemistry involved when a crystalline, fibrous substrate is chemically modified with a reagent introduced from a separate phase.

The general picture that develops suggests that the relative distributions of substituents at the 2-0-, 3-0-, and 6-0-positions of the D-glucopyranosyl units of cotton cellulose are the same for a specific nonreversible Williamson etherification conducted in solution or in mercerizing media. Evidence is rather pronounced for nonuniformity of attack by the reagent on the D-glucopyranosyl units along the molecular chain, even for those reactions conducted in mercerizing media (2,4). Apparently, all of the individual D-glucopyranosyl units are not uniformly accessible, a condition that has been assumed in certain studies (34).

Increasing the size of the reagent molecule in a Williamson etherification of cellulose in a mercerizing medium causes an increase in the proportion of substitution at the 6-0-position. This indicates that the hydroxyl group at C-6 is more sterically available in mercerizing media. Furthermore, increasing the size of the reagent molecule decreases the degree of random attack among the D-glucopyranosyl units from methyl chloride to ethyl chloride to dimethyl sulfate (3,5,7).

Nonreversible etherification of cotton cellulose, conducted in basic media below mercerizing strength, provides evidence that the hydroxyl group at C-2 is more available (relative to the hydroxyl group at C-6) for reactions as the swelling strength of the medium decreases (as the concentration of the sodium hydroxide decreases). Thus, the hydroxyl group at C-2 appears to be inherently more accessible than those at C-3 or C-6 for reactions conducted in media whose swelling capacity for cellulose is limited to that of water alone. The patterns of reactivity of different types of hydroxyl groups and different D-glucopyranosyl units in nonmercerizing media are consistent with (and perhaps indicative of) the chemical behavior expected for specific types of hydroxyl groups on highly ordered surfaces of crystalline microfibrils or bundles of microfibrils.

Reversible reactions introduce an additional dimension into the chemistry of the hydroxyl groups of cellulose. Substantial differences in the position of substituents result from conducting the reaction under rate-controlled conditions, on the one hand, or equilibrium-controlled conditions, on the other hand. Thus, a "wet-cure" type of reaction generally favors an equilibrium-controlled distribution of substituents (predominantly at the 6-0-position), whereas a "dry, bake-cure" type of reaction favors a rate-controlled distribution of substituents (increasingly toward the 2-0-position).

Conditions that accelerate the rate of the chemical reaction or that decelerate the rate of diffusion into the fiber cause a disproportionate amount of reaction to occur in the peripheral regions of the fibers. This type of variation in distribution has a pronounced effect on the performance properties (primarily wrinkle resistance) of chemically modified cotton fabrics. However, the detailed and quantitative effects of this variation, like the effect of variations in site of attachment to the D-glucopyranosyl unit and the site of reaction on or in the microfibril, need further clarification.

Chemical and analytical data indicate that the sites of attachments of substituents or cross-links at the 2-0-, 3-0-, and 6-0-positions of the D-glucopyranosyl units, on the surface or in the interiors of the microstructural units, and in the peripheral regions or in the interiors of the fibers are functions of the type of reaction (reversible or nonreversible), the nature and size of the specific reagent, the rate of the reaction, the rate of diffusion of reagent into the fibers, and the swelling power of the medium. Although there is need for much additional quantitative information on reactions of cotton cellulose, present knowledge makes possible the exercise of considerable control in the disposition of substituents or cross-links in cotton cellulose for the development of superior performance properties.

REFERENCES

1. Araki, M. 1964. Wood Res. (Kyoto) 33: 1-7, 8-15.

2. Cirino, V. O., Bullock, A. L., and Rowland, S. P. 1968. A Method of Measuring the Distribution of Substituents in Methyl Vinyl Sulfone-Treated Cotton Celluloses by Thin-Layer Chromatography. Analyt. Chem. 40: 396-399.

3. Croon, I. 1958. The Distribution of Substituents in Partially Methylated Celluloses. Part 3. Heterogeneous Reaction with Methyl Chloride. Svensk Papperstid. 61: 919-921.

4. ________. 1960. The Distribution of Substituents in Cellulose Ethers. Svensk Papperstid. 63: 247-257.

5. ________, and Flamm, E. 1958. The Distribution of Substituents in Ethyl Cellulose. Heterogeneous Reaction with Ethyl Chloride. Svensk Papperstid. 61: 963-966.

6. ________, and Lindberg, B. 1956. An Investigation of the Distribution of Substituents in Hydroxyethylcellulose. Svensk Papperstid. 59: 794-799.

7. ________, and Lindberg, B. 1957. The Distribution of Substituents in Partially Methylated Celluloses. Part 1. Homogeneous and Heterogeneous Reaction with Methyl Sulphate. Svensk Papperstid. 60: 843-849.

8. ________, and Purves, C. B. 1959. The Distribution of Substituents in Partially Substituted Carboxymethyl Cellulose. Svensk Papperstid 62: 876-882.

9. Fedorova, A. F. and Rogovin, Z. A. 1963. J. Polymer Sci. (USSR) 4: 1189-1194.

10. Frick, J. G., Jr., Pierce, A. G., Jr., and Tripp, V. W. 1962. Cross-Linking Cotton in the Peripheral Regions of the Fiber. Textile Res. Jour. 32: 425-426.

11. Gascoigne, J. A. and Gascoigne, M. M. 1960. Biological Degradation of Cellulose. 264 pp., illus. London.

12. Gogek, C. J. and Valco, E. I. 1967. Control of Radial Distribution of Cross-Links in Cotton Fibers. Textilveredlung 2: 423-428.

13. Guthrie, J. D. 1962. Imparting Wrinkle Resistance to Cotton Fabrics with Vapor from HCL-Paraformaldehyde. Amer. Dyestuff Reptr. 51: 507-512.

14. Haworth, S., Roberts, J. G., and Robinson, R. M. 1967. The Effects of Chemical and Physical Modification of Cotton on Cross-Linking. Textilveredlung 2: 361-365.

15. Hearle, J. W. S., and Peters, R. H. 1963. Fiber Structure. (a) 216-220; (b) 221-222. London.

16. Hoiness, D. E., Wade, C. P., and Rowland, S. P. 1968. The Synthesis and Identification of Allyl Ethers of Glucose and Cellulose. Canad. Jour. Chem. 46: 667-672.

17. Jeffries, R., Roberts, J. G., and Robinson, R. M. 1968. Accessibility and Reaction Sites in Cotton. Textile Res. Jour. 38: 234-244.

18. Joarder, G. K., Brannan, M. A. F., Rowland, S. P., and Guthrie, J. G. 1968. An Uncatalyzed, Vapor-Phase Cross-Linking Reaction of Cotton Cellulose with Formaldehyde. Textile Res. Jour. [In Press].

19. Leonard, N. J., and Paukstelis, J. R. 1965. Small Charged Rings. VII. Interconversion of Substituted β-Chloroethylamines and Aziridinium Salts. Jour. Org. Chem. 30: 821-825.

20. Lukanoff, T. 1965. On the Cyanoethylation of Cellulose. 3rd Comm: The Distribution of Substituents in Cyanoethyl Cellulose. Faserforsch. Textiltech. 16: 540-546.

21. Patel, S., Rivlin, J., Samuelson, T., Stamm, O. A., and Zollinger, H. 1968. Investigations on the Chemical Constitution of Cotton Cross-Linked with Formaldehyde. Textile Res. Jour. 38: 226-234.

22. Roberts, E. J., and Rowland, S. P. 1967. Effects of Selected Reaction Conditions and Structural Variations on the Distribution of 2-(Diethylamino)Ethyl Groups on D-Glucopyranosyl Residues of 2-(Diethylamino)Ethylated Cellulose, Starch, and The Anomers of Methyl 4,6-O-Benzylidene-D-Glueopyranoside. Carbohyd. Res. 5: 1-12.

23. ________, and Rowland, S. P. 1967. Synthesis of Mono-0-(2-diethylaminoethyl)-D-Glucoses and Distribution of Substituent Groups in 0-(2-Diethylaminoethyl)-Cellulose. Canad. Jour. Chem. 45: 261-265.

24. Roberts, E. J., and Rowland, S. P. 1968. Distribution of Substituent Groups in O-(2-Aminoethyl)Cellulose. Canad. Jour. Chem. [In Press].

25. Rowland, S. P., Bullock, A. L., Cirino, V. O., and others. 1967. The Relative Reactivities of the Hydroxyl Groups of Cotton Cellulose—A Progress Report. Textile Res. Jour. 37: 1020-1030.

26. ________, Bullock, A. L., Cirino, V. O., and Wade, C. P. 1968. Reagent Effects on Distribution of Methylsulfonylethyl Substituents in The D-Glucopyranosyl Unit of Cotton Cellulose. Canad. J. Chem. 46: 451-457.

27. ________, Cirino, V. O., and Bullock, A. L. 1966. Structural Components in Methyl Vinyl Sulfone Modified Cotton Cellulose. Canad. Jour. Chem. 44: 1051-1058.

28. ________, Cousins, E. R., and Mitcham, D. 1965. Variations in Crosslink Organization in Formaldehyde-Modified Cotton Celluloses. Jour. Appl. Polymer Sci. 9: 3869-3885.

29. ________, and Post, A. W. 1966. A Measure of Effective Crosslinks in Formaldehyde-Modified Cotton Celluloses. Jour. Appl. Polymer Sci. 10: 1751-1761.

30. ________, Rollins, M. L., and deGruy, I. V. 1966. Degrees of Heterogeneity of Distribution of Formaldehyde Crosslinks in Cotton Cellulose. Jour. Appl. Polymer Sci. 10: 1763-1776.

31. Smith, B. F. 1965. Determination of the Distribution of the Methoxyl Groups in Methylated Cellulose. Univ. Microfilms 66-9506: 18-20, 127-129.

32. Spurlin, H. M. 1939. Arrangement of Substituents in Cellulose Derivatives. Jour. Amer. Chem. Soc. 61: 2222-2227.

33. Timell, T. 1960. Studies on Cellulose Reactions. Stockholm, Roy. Inst. Technol. 198-199.

34. Touzinsky, G. F. 1965. The Substituent Group Distribution in a Michael Reaction. Carbamoethyl Cellulose. Jour. Org. Chem. 30: 426-428.

35. Wade, C. P., Roberts, E. J., and Rowland, S. P. 1968. Selective Accessibilities of the Hydroxyl Groups at C-2, C-3, and C-6 in the D-Glucopyranosyl Units of Cotton Cellulose. Jour. Polymer Sci. [In Press].

36. Willard, J. J., Turner, R., and Schwenker, R. F., Jr. 1966. Chemical Structure of Resin-Treated Cellulose. Part II: Trimethylolmelamine Bonding with Cotton. Textile Res. Jour. 36: 1051-1055.

37. ________, Valko, E., and Tesoro, G. C. 1968. Relationship between Radial Distribution of Crosslinks in Cellulosic Fibers and Fabric Performance. [Presentation. The Fiber Society Meeting, April 18-19.]

EXPLORATORY STUDIES ON VAPOR PHASE ENCAPSULATION OF COTTON FIBERS. II. POLYOXYMETHYLENE

[SUMMARY]

by
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(Presented by W. Brenner)

Vapor phase treatments are receiving increasing interest for the upgrading of cotton fabrics. Experiments have been carried out on the modification of the properties of cotton fabrics with high molecular weight polyoxymethylenes. Techniques are described for accomplishing the deposition of high molecular weight polyoxymethylenes from formaldehyde vapor onto cotton fabrics and data are presented on the character of these polymer deposits and certain physical properties of the coated fabrics.

High molecular weight polyoxymethylene polymer deposits were obtained by immersion of cotton fabrics in a suitable alkaline catalyst solution at ambient temperatures and then exposing the catalyzed cloths to monomeric formaldehyde vapor. A typical catalyst system consisted of t-butylamine and diphenylamine dissolved in a halogenated solvent such as carbon tetrachloride. The formaldehyde vapor was generated by heating a paraformaldehyde slurry in paraffin oil at 115° to 120° C. Polyoxymethylene polymer coatings were deposited on the surfaces of the cotton fiber in amounts depending upon such reaction variables as formaldehyde vapor concentration, reaction time, and temperature. Polymer deposits ranging from as little as 2 percent to over 50 percent based upon the weight of the cotton fabrics could be reproducibly obtained by varying reaction conditions. Typically 10-percent polymer add-ons could be obtained in approximately 10 minutes' exposure time with one rather convenient set of reaction conditions.

The polyoxymethylene deposits were isolated by solvent extraction and identified by infrared and chemical analysis. Photomicrographic studies were carried out to ascertain the location of these polymer deposits on the fibers. Differential staining of cross section of fiber specimens shows that the polymer deposits are located along the outer periphery of the fibers.

As is well known polyoxymethylenes require end capping to enhance their thermal stabilities. This was accomplished by reacting polyoxymethylene hydroxyl groups with acetic anhydride, which treatment apparently decreased the solubility of the cotton fibers in cupriethylenediamine. Experiments with difunctional anhydride reagents are in progress.

Physical strength measurements have been made on such polyoxymethylene polymer modified cotton fibers and are continuing. Preliminary results on numerous test samples show no loss in tensile strength and tear resistance, improved elongation and enhanced abrasion resistance over a large range of polymer loadings. These results compare favorably with acid catalyzed formaldehyde cotton treatments which generally result in substantial losses in the strength properties of cotton fabrics.

DISCUSSION

Question: Do you have any information on the hand of these fabrics?

Dr. Brenner: Up to approximately 10-percent weight gain of polyoxymethylene on the fabric, the hand is similar to that of cotton. At higher levels of polyoxymethylene there is stiffness and development of color.

Question: What fabric was used in these studies?

Dr. Brenner: The fabric was an 80^2 printcloth supplied by the U.S. Department of Agriculture.

SWELLABILITY OF CROSSLINKED COTTONS

by
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ABSTRACT

The alkali centrifuge values (ACV's) permit the swellabilities of cotton fibers to be characterized quantitatively in terms of sorption of caustic solution of mercerizing strength. Durable-press cotton samples were evaluated by the alkali swelling centrifuge test. The resultant ACV's emphasized the varied alterations in intrafiber structure that were achieved by crosslinking cottons. In general, crosslinking reduced the swelling capacity of the fibers—by as much as 80 percent in one process. Certain conditions or stages in some treatments produced increased sorptivity. The alterations in ACV were dependent upon various factors in the processes, for example, cross-linking agent, degree of modifications, method of treatment, catalyst, and curing temperature.

INTRODUCTION

The alkali swelling centrifuge test, developed by Marsh and others[1] measures the swellability of fibers in terms of the sorption of 15-percent sodium hydroxide solution. The alkali centrifuge value (ACV) is the percent increase in weight of a specimen that was soaked in the caustic solution and centrifuged under specified conditions. The ACV's permit quantitative comparison of the changes in sorptivity induced by various agents.

The ACV's of native cottons vary with the morphology of the fibers because the fullness of the secondary wall controls the swelling into the fiber lumen while an intact cell wall limits the outward swelling.[1],[2] However, the restraining power of impaired primary cell walls is diminished and swelling is enhanced, or the ACV is increased. Therefore, the damage caused by a deteriorative mechanical or chemical agent can be assessed from the magnitude of the ACV increase.

Conversely, a counteracting force impedes the swelling. The external restraint imposed by yarn twist and fabric weave prevents the fibers from swelling

[1] Marsh, P. B., Merola, G. V., and Simpson, M. E. Experiments with an Alkali Swelling-Centrifuge Test Applied to Cotton Fiber. Textile Res. Jour. 23: 831-841. 1953.

[2] Landstreet, C. B. Alkali Centrifuge Test. A Study of Test Methods. Textile Bull. 90(2): 38-41, 44. 1964.

to their fullest capabilities; the resultant decrease in ACV reflects the extent of the restriction.[3] Chemical crosslinkages exert an internal restraint when they reduce the mobility of the fiber elements and the accessibility to intrafiber regions. A quantitative measure of such restrictions furnishes information of importance to the effectiveness of subsequent treatments which are dependent upon the ability of the fibers to sorb liquids or to swell. For example, aftermercerization can have little effect if the caustic solution does not adequately penetrate the restrained fibers.

As indicated above, many factors influence ACV's. Therefore, the maximum usefulness of the test is obtained on a comparative basis; that is, the ACV of the treated cotton is compared with the ACV of the cotton as it occurs immediately prior to the treatment under consideration. For fabric samples, the restraints due to fabric weave and yarn twist can be mitigated if the yarns are stripped from the fabrics and are cut into short lengths (about one-half to one inch). Finally, the variability among replicate determinations can be minimized by proper attention to procedural details[3].

This report illustrates that crosslinked cottons can be characterized with the alkali centrifuge test. The ACV's show that the sorptivity of fibers was variously altered by different crosslinking agents, by the degree of crosslinking, by the method of treatment, and at intermediate steps in noncontinuous processes.

Sorption data were determined on samples of printcloth crosslinked with formaldehyde to different degrees and by five different methods in which hydrochloric acid was used as the catalyst. Two illustrative series are shown in figure 1. The "Form W" had been prepared in an aqueous medium and the Form D in an acetic acid solution. The desized, scoured, and bleached control had an ACV of 265. The extremely wide range in ACV (310 to 50) for the treated samples emphasized the variations produced by the crosslinkages—from increased sorptivity to drastic reduction in caustic sorption. When the crosslinks were introduced into the water-swollen fibers, the ACV rose rapidly to a maximum of 310 at about 0.25 percent formaldehyde and then decreased as the formaldehyde percentage was increased. The introduction of crosslinks into the nonswollen fibers of the Form D method produced a continuous decrease in ACV until a plateau was reached at about 1.5 percent formaldehyde and an ACV of 50. This is an extremely low value and is only slightly higher than the 10 to 20 range observed for interfiber sorption when glass fibers were tested.

Except as noted above, the ACV decreased with increasing formaldehyde content in all samples tested. However, the diverse relationships between ACV and formaldehyde indicated that various alterations in caustic sorption were effected by the method of introducing the crosslinking agent. Therefore, the

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[3] Honold, E., and Grant, J. N. A Method for Characterizing Cottons. Textile Indus. 1968. [In Press].

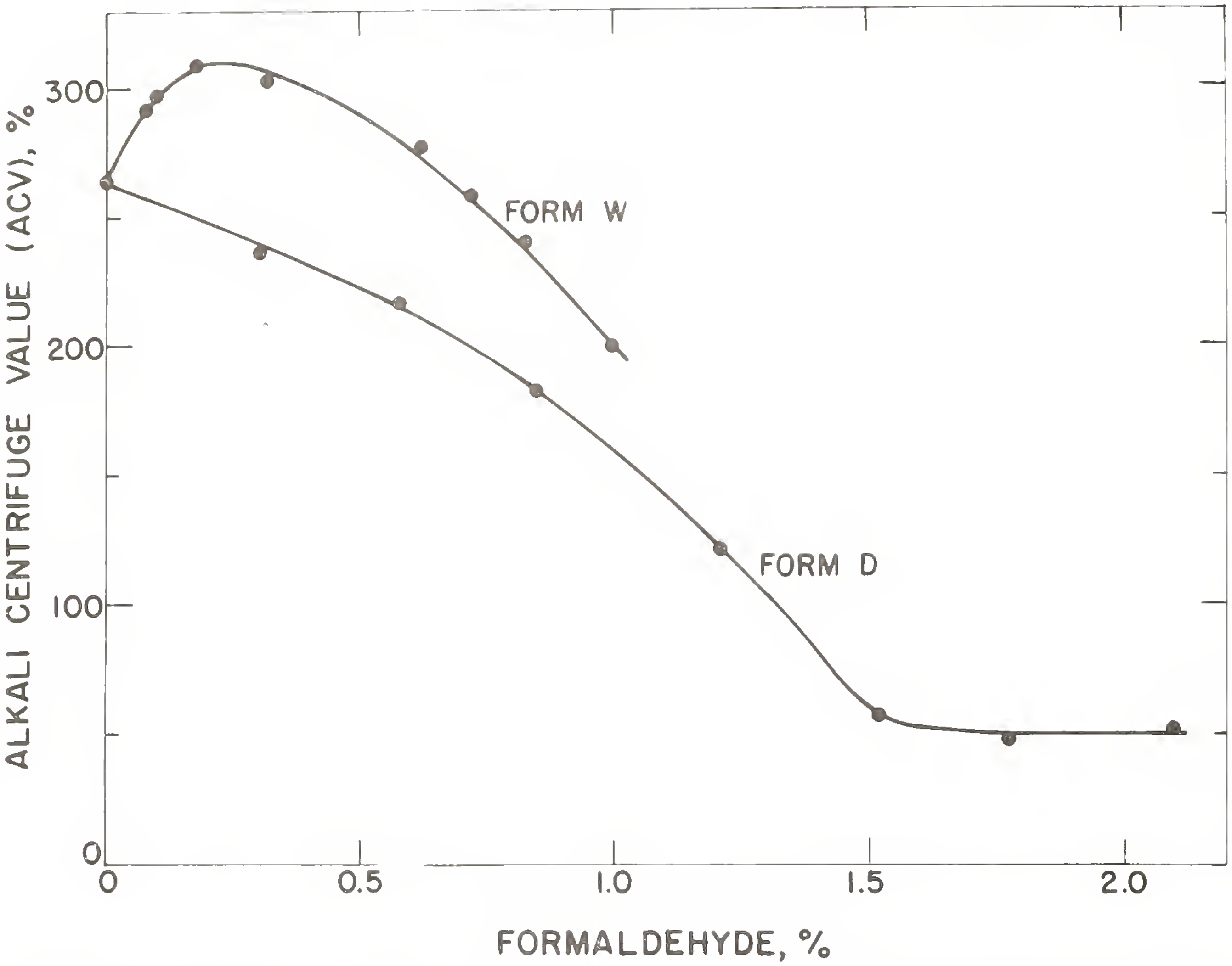

Figure 1.—The influence on alkali centrifuge value of the degree of crosslinking with formaldehyde in samples prepared in a Form-W or Form-D medium.

alkali centrifuge test differentiated among the methods of preparing the formaldehyde crosslinked cottons.

The percentage of sodium hydroxide in the weight increase was found, by titration, to be higher than that in the soaking solution. This is in agreement with the well-known fact that sodium hydroxide is preferentially adsorbed by cotton fibers. Up to 1-percent formaldehyde, there were no observable differences among all five series in the calculated weights of preferentially adsorbed sodium hydroxide. In this range, the average value decreased from 10.5 grams per 100 grams of sample for the uncrosslinked control to 8 grams at 1 percent formaldehyde.

The portion of sodium hydroxide that is preferentially adsorbed is related, in these treated cottons, to the intrafiber elements that are accessible to the caustic solution for conversion to Cellulose II. Therefore, the extent of conversion of crystalline form during the test should be reflected in the increases in standard moisture regains of the tested specimens. Subsequent to the alkali centrifuge test, the regains were determined after the specimens had been neutralized, washed, dried, and reequilibrated under standard atmospheric conditions. In all series, these regains for the specimens of less than 1-percent formaldehyde were higher than that of the uncrosslinked control. A maximum post-test regain was reached at about 0.3 percent formaldehyde and thereafter the values decreased until the original pre-test regains were approached in the 1.5 percent to 2.0 percent formaldehyde range. The latter observation confirms the relative inaccessibility to the caustic solution of the more highly crosslinked samples because the post-test regains are only slightly greater than the pre-test regains.

Samples crosslinked with different agents are being investigated and preliminary results indicate that additional variables also affect caustic sorption, for example, variety of cottons, catalysts, and differences in the technical details of the treatment processes. Some of these results are discussed briefly in the following paragraphs.

Scoured, plain-weave fabrics from cottons of different varieties (Deltapine-15, Hopi-Acala, Pima S-2) were simultaneously treated with a Permafresh to about 5-percent add-on. The data in table 1 show that the Deltapine was most highly crosslinked and had the greatest reduction in ACV after it was crosslinked. Less restriction in sorption was developed in the Hopi-Acala and Pima cottons since the reductions in ACV were considerably less than that of the Deltapine.

Fabrics were obtained that had been

Table 1.—ACV's of crosslinked cottons of different varieties

Cotton varieties	Nitrogen	ACV		
		Scoured	Cured	Δ
	Pct.			
Hopi-Acala	0.67	207	179	28
Pima	0.63	234	196	38
Deltapine	0.73	242	165	77

Agent: Permafresh to about 5-percent add-on.

Catalyst: A buffered zinc nitrate.

prepared by the Wet Fixed method, one of the two-step procedures recommended for durable-press treatment. Specimens at each step (before and after curing) were tested. One general conclusion was reached—the deposition of agent caused a decrease in ACV and curing induced an additional decrease. This conclusion is illustrated below for one set of samples.

ACV's at stages in the wet fixed process:

Control	259
Wet fixed only	193
Cured at 149° C.	106
at 160° C.	70

Agents: Combination of an Aerotex and a Fixapret.

Add-on: About 11.5 percent.

Catalyst: $MgCl_2$.

These data also show that the temperature of curing affects the caustic sorption because the finished sample after curing at 149° C. had an ACV of 106 as compared with an ACV of 70 after curing at 160° C.

Tests were made on several groups of samples that had been prepared by the Polyset method, a two-step process developed at the SURDD. A sateen was crosslinked to different degrees in an Aerotex or a Permafresh medium in which either zinc acetate plus acetic acid or zirconium acetate was used as the catalyst. Illustrative data are given in table 2 for the two crosslinking agents combined with each of the two catalysts. These four samples were chosen to represent this method because of their comparable add-on percentages. All samples prepared by this method were tested before and after curing. Following the

Table 2.—ACV's at stages in the Polyset process

Treating agent and catalyst	Add-on	Alkali centrifuge value after—	
		Step 1, deposition	Step 2, curing
	Pct.		
Permafresh:			
Zr acetate	5.8	248	231
Zn acetate [1]	5.9	259	206
Aerotex:			
Zr acetate	6.4	224	184
Zn acetate [1]	6.2	155	121

[1] Acetic acid was added to the zinc acetate catalyst.

Mercerized control: ACV of 232.

deposition step in all the Permafresh samples of different add-ons and with either catalyst, the ACV was 7 to 27 units higher than that of the uncrosslinked control. In three sets out of four in the Aerotex groups, the ACV was lower than the control by 8 to 86 units. The Aerotex appears to produce more restriction to swelling than the Permafresh. After curing at 160° C. the ACV decreased from that of the deposition step in each instance. Permafresh with the zirconium acetate catalyst yielded values equivalent to that of the mercerized, uncrosslinked control. All other combinations produced considerably lower values, from 24 to 111 units less than the control.

CONCLUSIONS

Many factors in the preparation of crosslinked cottons alter the caustic sorption of the product. Considerable information can be obtained from this simple and relatively rapid alkali-swelling-centrifuge test for crosslinked cottons relative to their sorptivity, a property that becomes important in certain subsequent treatments. The utility of the test lics in the fact that numerical values are obtained, which permit quantitative comparisons of the effects of crosslinking agents, methods of treatment, degree of crosslinking, and various other parameters involved in the preparation of crosslinked fabrics.

ACKNOWLEDGMENT

The author wishes to express appreciation to Norman Hollis of the Harris Research Laboratories for supplying the Wet Fixed samples, and to the following persons at the Southern Utilization Research and Development Division. Stanley R. Rowland for supplying the formaldehyde samples, and Albert S. Cooper, Jr., for supplying the Polyset samples.

ATTACHMENT OF TEXTILE FINISHING AGENTS TO COTTON AS CROSSLINKED POLYMER FILMS

[SUMMARY]

by
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The permanent alteration of the textile properties of cotton is conventionally accomplished by such methods as cellulose swelling, substitution, grafting, and crosslinking. Each of these processes alters the chemical and physical structure of cotton cellulose, and adversely affects some of the properties of cotton while improving others. Many of the simplest substitution and grafting processes tend to be slow, unsuitable for continuous fabric treatment, and uneconomical for textile finishing. Yet, the traditional view persists that covalent bond formation between finishing agent and cellulosic substrate is essential for complete durability of the attached agent. Recent developments show, however, that the permanent attachment of monomers and polymers to cotton can be effected without chemically or physically altering the cellulose. The processes to be described involve the deposition of polymers in or around individual fibers of a fabric and crosslinking the polymer without crosslinking or grafting the cellulose.

The present studies include such varied types of polymers as low-density polyethylene, silicones, and polyepoxide condensates. For the application of preformed polymers to cotton, free radical-induced crosslinking has proved effective. Fabric impregnated with the polymer and an organic peroxide is heat-cured for a few minutes to form a vulcanized film of the polymer around the individual fibers. An example of this type of process is the application of low-density, highly branched, high-molecular-weight polyethylene, which undergoes crosslinking at tertiary carbon atoms in the presence of benzoyl peroxide. Certain commercially available polyethylene latexes were observed to crosslink rapidly even at temperatures as low as 100 to 130° C. The properties of the treated fabrics are still being characterized, but it has already become evident that the wet tensile strength of nonwoven webs may be increased as much as eightfold without altering the dry strength of such materials. Less than a twofold increase in wet strength is produced if the polyethylene is merely deposited on the web in noncrosslinked form.

The wash-wear finishing of cotton with peroxide-crosslinked dimethyl silicone, as developed earlier at this laboratory, has been further studied. Various combinations of silicone and N-methylol agents have been examined which impart durable press properties in the absence of added Lewis acid catalysts. Under these conditions, the N-methylol agents impart only a very low level of crosslinking in the cellulose itself, resulting in high retention of strength and abrasion resistance in the fabric. The crosslinked silicone forms an elastomer film around the fibers, imparting both resilience and lubricity. The level of silicone required to obtain wrinkle recovery angles of 300° or higher has been reduced to 2.5 to 5.0 percent, making the method more competitive costwise with conventional resin finishing processes.

By contrast to the above processes, the in situ formation of crosslinked polymers within cotton fibers permits the attachment of monomeric textile finishing agents, such as dyes, to cotton. As an example of this method, the use of commercially available tetraepoxide, allyl glycidyl ether tetramer, is described. The tetraepoxide readily forms three-dimensional network polymers by reaction with compounds containing at least two active hydrogen atoms per molecule. This type of crosslinking proceeds by ionic mechanisms. If the dye to be used contains at least two -NH- or -OH groups per molecule, it is rapidly bonded to the fabric when cured with the epoxide at 130° to 160° C. Amine dyes serve as their own catalyst, while phenolic dyes require added weak-base catalysts. At temperatures below 140°, the treated cellulose remains completely soluble in cupriethylenediamine, showing that it has not been crosslinked. At higher temperatures, a small amount of cellulose insolubility and crosslinking is observed. The same procedure may be used to attach dyes to glass fabric or other inert substrates, again showing that grafting to the substrate is not required.

High efficiency of dye attachment is obtained at tetraepoxide concentrations in the range of 0.4 to 1.6 percent, for a dye concentration of 0.5 percent. That the dye is incorporated by the epoxide in a network polymer is shown by the dependence of dyeing efficiency on dye/epoxide mole ratio. At too high or too low ratios, simple nonpolymeric adducts are formed. Likewise if the dye contains but one active hydrogen atom per molecule, no dye polymer is formed unless an auxiliary crossbonding agent, such as sodium sulfide, is provided as a means of joining tetraepoxide molecules. In the latter instance, the dye molecules are attached as pendant groups to the crosslinked polymer backbone. Because of the extremely stable polymers that the tetraepoxide forms with amino and hydroxylic dyes, the bonded dyes apparently cannot be extracted by mineral acids, bases or organic solvents, unless conditions are used which decompose the cellulose. The further extension of these methods to other areas of fabric finishing, such as flameproofing, soil resistance and water repellency, is currently under investigation.

COTTON CELLULOSE–POLY(VINYL) COPOLYMERS
[SUMMARY]

by
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Using electron spin resonance and physical property measurements, information has been obtained concerning the mechanism of formation and the nature of free radicals in cellulose initiated by interaction with ionizing radiation, by reaction of ceric ions in acidic solution, or by hydrogen abstraction by hydroxyl radicals formed on reaction of ferrous ions with hydrogen peroxide in aqueous solutions. The graft copolymerization reactions of vinyl monomers with activated fibrous cotton cellulose have also been investigated by electron spin resonance. Some of the physical properties of fibrous cellulose are changed by grafting with vinyl monomers. Fibrous cellulose graft copolymers are produced which have thermoplastic, rot resistance, abrasion resistance, and increased delayed elastic recovery properties.

Free Radicals–Energy localization from ionizing radiation in the cellulose molecule resulted in depolymerization, dehydrogenation, and destruction of glycopyranoside units to yield gaseous products, of H, CO, and CO_2. The dehydrogenation and depolymerization reactions initiated the formation of both short-lived and trapped free radicals on cellulose, crystalline lattice type I. The ESR spectrum of the trapped radicals consisted of three lines in an intensity ratio of about 1:1.8:1. Dehydrogenation at carbon C_5 of a glucopyranoside unit would give a free radical which could interact with the two equivalent protons on carbon C_6 to give a three-line spectrum. The delocalizing energy at carbon C_5, due to the presence of the ring oxygen atom, was greater than that at any other position; therefore, this was considered the most probable site of the trapped free radical. The G-value for trapped radicals was about 1.4; the initial yield of short-lived radicals was about 1.5 to 2 times that for trapped radicals.

Ceric ion in acidic solution reacted with cellulose to yield a short-lived free radical which generated a broad, unsymmetrical single-line ESR spectrum. Ceric ion probably formed a complex with the cellulose molecule by reaction through the hydroxyl groups on carbon C_2 and C_3. There was a single electron transfer from the cellulose molecule to Ce^{IV}. Then Ce^{IV} was reduced to Ce^{III}, followed by release of Ce^{3+} and anhydroglucose ring cleavage of the C_2-C_3 bond. A short-lived free radical was then formed on either carbon C_2 or C_3.

When cellulose was immersed in an aqueous solution of $Fe(NH_4)_2(SO_4)_2$, dried in a stream of nitrogen, then immersed in an aqueous solution of H_2O_2, and immediately followed by freezing in liquid nitrogen, an ESR spectrum of a short-lived free radical could be recorded at temperatures lower than -110° C. The ESR spectrum, although low in intensity, appeared to be three lines and could be attributed to a free radical formed on abstraction of the hydrogen atom from the hydroxyl group of carbon C_6 or the hydrogen atom from carbon C_5 by the ·OH radical generated by the reaction of Fe^{2+} with H_2O_2.

Grafting—Two important factors in initiating graft copolymerization reactions of vinyl monomers with activated cellulose are: The lifetime of the free radicals and the accessibility of the free radicals to the monomers. In the case of ceric ion initiation or hydroxyl radical initiation, the lifetime of the free radicals on the cellulose molecule are short; therefore, the monomer should be present when the free radicals are formed. In the case of ionizing radiation both short-lived and trapped-free radicals are formed. Consequently, the activation reaction and the copolymerization reaction can either be conducted simultaneously or consecutively. The short-lived radicals formed are probably not too important in the copolymerization reaction, since they would likely be quenched by the solvent for the monomer. In the case of the trapped radicals, considering both the crystalline structure and macrostructure of fibrous cellulose, the rate of diffusion of monomer to the free radical site is an important factor in the copolymerization reaction.

During the copolymerization of vinyl monomers with irradiated cellulose, the intensity of the ESR spectrum of the irradiated cellulose decreased. However, even after a lapsed time as long as 17 hours, a measurable fraction of the trapped radicals initially formed in the irradiated cellulose remained. About 35 to 40 percent of the initial concentration of trapped radicals were apparently located within the highly ordered or crystalline region of the fibrous cellulose and were not accessible to monomer solution. In the case of ceric ion initiated copolymerization reactions of vinyl monomers with cellulose, the ESR spectrum changed from a broad single-line to a three-line spectrum. In the case of the ·OH radical initiated reactions, the ESR spectrum changed from a three-line spectrum to a spectrum which appeared to be a combination of two single-line spectra.

Properties—The molecular weights of the grafted polymers were varied over a range from about 3 x 10^4 to 1 x 10^6. Using chemical redox initiation, generally one or more grafted molecules were obtained per cellulose molecule. Using ionizing radiation, generally less than one grafted molecule was obtained per cellulose molecule. The distribution of the grafted polymer in the fibrous structure was determined by the experimental conditions during the copolymerization reactions. Variations were obtained in the shape of the fibrous cross-section from rounded to collapsed, in layering effects in the fiber, and in the location of grafted polymer in the fiber either uniformly distributed, concentrated in the surface, or concentrated in the center.

FOURTH SESSION: V. C. Smith, Collins & Aikman Corp., Albemarle, N. C., Chairman

ROT RESISTANCE OF COTTON FABRIC TREATED WITH VARIOUS FLAME RETARDANTS

by
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(Presented by R. M. Perkins)

ABSTRACT

Several durable flame retardant finishes were applied (using either a heat cure or a chemical fixation technique) to three different cotton fabrics at various add-ons, and evaluated for rot resistance. In general, the heat-cured samples afforded better resistance to micro-organism attack than the chemically fixed ones. One APO-THPC treated sateen sample with about 30-percent add-on retained over 100 percent breaking strength after three months, and a THPC-MM sample (20-percent add-on) retained 76-percent strength after 3 months. The treated samples having the best rot resistance also offered some protection against acid and had improved dimensional stability.

INTRODUCTION

Several durable flame retardant treatments have been developed at the Southern Utilization Research and Development Division (SURDD) for application to cotton materials. In other studies finishes have been applied to make rot resistant cotton fabrics. In some exploratory work on flame retardant fabrics, it was found that in addition to flame resistance, certain finishes also impart rot resistance, dimensional stability, wrinkle recovery, resistance to yellowing, or improved strength. No single finish, however, imparts all of these desirable properties to cotton fabric, nor is a single finish applicable to all types of fabric construction.

The object of this study was to apply several durable reactive-type flame retardants developed at SURDD to three different fabrics at various add-ons, and to evaluate the properties, especially with respect to resistance to micro-organisms as measured by the rot bed test (3).

EXPERIMENTAL

The three fabrics selected for this study were a 48 x 48 scoured and bleached sheeting, an 8 oz. lined duck, and an 8 oz. OD sateen. Five treating solutions were used: three were based upon THPC (5) and two upon THPOH (2). THPOH (tetrakis [hydroxymethyl] phosphonium hydroxide) is the reaction product of NaOH and THPC (tetrakis [hydroxymethyl] phosphonium chloride). These are combined either with APO (tris [1-aziridinyl] phosphine oxide) or with MM (trimethylol melamine). Three of the treatments were accomplished by means of a pay-dry-cure technique; two treatments chemically fixed the polymer inside the cotton when the impregnated fabric was exposed to NH_3 gas.

For the heat-cured treatments the following formulations were used:

1. APO-THPC at 10-, 20-, 30-, or 40-percent total solids.
2. THPC-MM-urea at 9-, 18-, and 36-percent total solids.
3. THPOH-MM-urea at 34-percent total solids.

The chemically fixed samples were treated with a THPC-urea precondensate followed by exposure to NH_3 gas, or by padding the fabrics through a 25-percent solution of THPOH and exposing to NH_3 gas—once for the lower add-on, and twice for the higher. Both the THPOH treating solutions were alcoholic-aqueous mixtures, although in current work completely aqueous solutions are being used.

TESTING

Physical testing was performed by ASTM methods: breaking strength, 1-inch strip method (1a); crease recovery, Monsanto method (1b), and on wet fabrics according to the procedure of Lawrence and Phillips (4); flame-resistance, standard-vertical method (1c); and air permeability (1d).

Phosphorus was determined by an X-ray fluorescence method using a General Electric XRD-5 diffractometer modified for fluorescence analysis (7).

Dimensional stability of the sheeting samples was determined after one and five launderings made in an agitator-type home machine followed by tumble drying. Measurements were taken in the warp and filling directions, and the percent shrinkage calculated from these.

Acid resistance was determined on the sateen samples. Ravelled strip samples were prepared; across each strip 10 percent or 40 percent H_2SO_4 was applied with a dropper. The wetted sample was allowed to dry either 24 or 48 hours, then it was neutralized with 10 percent NaOH, washed in cold and finally hot running tapwater, and air dried. Breaking strength determinations were made, and the strength retained calculated.

To test the rot resistance, a composted soil was prepared by mixing equal parts of fertile topsoil, sand, and well-rotted stable manure. The temperature of the soil was maintained at 85° ± 1° F. and the moisture content was kept at 30 percent above the oven dry weight (3). Of the treated samples and controls, 1- by 6-inch ravelled strips were randomly laid on the soil and covered with more soil. The samples were buried five deep—each being separated by a layer of soil. Samples were removed after 1, 2, 4, 6, 8, 12, 16, and 20 weeks' burial and thoroughly washed in hot running tapwater, before testing for strength.

RESULTS AND DISCUSSION

The samples treated by the pad-dry-cure technique retained less breaking strength than those chemically fixed with NH_3. The NH_3 fixed samples retained all of the breaking strength and in some samples showed a slight increase. The heat-cured samples retained about 80-percent strength.

Some of the APO-THPC and THPC-MM samples had increased conditioned wrinkle recoveries. One APO-THPC treated sheeting sample with about 28 percent add-on had a conditioned recovery angle of 288° and a wet one of 216°, and a similar sateen sample had a conditioned recovery of 259° and a wet recovery of 232°. A THPC-MM sample with 29 percent add-on had a conditioned wrinkle recovery of 249°. The duck samples also had some increase in wrinkle recovery, but not as much as the sheeting or the treated sateen samples.

Air permeability decreased as the add-ons increased within each set of samples. The control sheeting had an air permeability rating of 58 $ft.^3/min./ft.^2$, and this was reduced to about half at the higher add-ons of the APO-THPC-MM samples. The NH_3 fixed samples had higher permeability values than heat-cured samples and were only slightly different from the control samples.

Some of the samples were purposely treated with solutions having low concentrations so that they would not pass the standard flame test, and then tested to determine whether or not these would have any significant degree of rot resistance.

At the higher add-ons, the APO-THPC and THPC-MM samples were stiff; however, no softeners had been used in the padding formulations nor as an aftertreatment. The type of fabric also played a significant role in the hand—the duck was considerably stiffer than the sheeting or the sateen.

The dimensional stability of some of the sheeting samples was determined after one and five home launderings and tumble dryings. The THPOH-NH_3 samples had relatively poor dimensional stability and were about the same as the untreated control. All of the other treated samples exhibited some improvement over the control; generally, the heat-cured samples were more stable than the NH_3 fixed.

It was believed that the fabrics treated with flame retardants that cross-linked the cellulose would afford more protection to acid attack than flame retardants that primarily formed a polymer. As the amount of flame retardant was increased, the protection of the fabric to acid attack was increased. Good protection was afforded by the APO-THPC treatment, and by the THPC or THPOH-MM-urea treatments. For example, at about 20-percent add-on, an APO-THPC sample spotted with 10 percent H_2SO_4 and dried 48 hours retained 81-percent breaking strength, the THPC-MM sample retained 90-percent strength, and the THPOH-NH_3 sample retained only 52-percent strength. Again, the NH_3 fixed samples were not as good as the heat cured samples.

Rot Resistance—There were only residual pieces of sheeting samples remaining after 4 and 5 months in the soil beds. After 3 months, the THPC-MM sample with 29-percent add-on retained 70-percent strength; a comparable APO-THPC sample about 16-percent retention. After 1 month in the rot beds, among the chemically fixed, none exhibited any significant strength retention.

Among the treated sateen samples, one sample that had been chemically fixed (THPC-urea precondensate) retained 38 percent strength after 2 months; the others were very degraded. The THPOH-NH_3 sample (20 percent add-on) retained only 9 percent strength after 1 month; a comparable APO-THPC sample (20 percent add-on) had 107 percent after 1 month, 41 percent at 4 months, and 9-percent at 5 months. In the treated sateen series, the APO-THPC and the THPC-MM samples with about 20-percent add-on retained about 77-percent strength after 3 months, 37-percent after 4 months, and less than 10-percent after 5 months. One APO-THPC sateen sample (30-percent add-on) retained over 100-percent strength after 3 months. These strength retentions are all based on the treated controls.

The treated duck samples had approximately the same resin add-ons as the treated sateen series; however, in general, the duck samples had less strength retention than the sateen. More rot resistance was imparted by a heat cured treatment; at comparable weight increases, there were no significant differences among the APO-THPC, THPC-MM or THPOH-MM samples.

The phosphorus content of the duck samples was measured before and after soil burial. The soil burial samples had been thoroughly washed in hot running tapwater to remove residual soil and hydrolyzed polymers. The THPOH-NH_3 sample with 22-percent add-on had 10.6-percent phosphorus; the APO-THPC sample with 29-percent add-on had 7.0-percent phosphorus. After 1 week in the rot beds, the APO-THPC sample had 6.4-percent P and the THPOH-NH_3 sample 10.3-percent P; both had excellent strength retention. However, after 1 month the P content of the APO-THPC sample was 3.8 percent and of the THPOH-NH_3 sample 4.3 percent, yet the former sample retained all of its breaking strength and the latter only 22 percent. This is another indication that the cellulose reactive polymer offers better protection than the nonreactive polymer, even though both treated samples contained essentially the same amount of P.

After the treated samples had been exposed to the action of the soil beds, thoroughly washed, and tested to determine strength retention, parts of the breaking strips were submitted to the match test to determine flame resistance (6). In general, if a sample has a 135° to 145° angle in the match test, it will pass the standard vertical flame test. Only the APO-THPC treated samples at 20 to 30 percent add-on would still pass the standard vertical flame test after 2 months' soil burial and, in fact, would also pass it after 5 months' burial. Once again we see the advantage of some cellulose reaction to impart additional properties to these flame resistant fabrics.

SUMMARY

Five durable flame-retardant finishes were applied to three cotton fabrics giving a range of add-ons. The resistance to micro-organism attack, as measured by the rot-bed-test, was evaluated. In general, the heat cured samples afforded better resistance than the chemically fixed ones. At about the same add-on, there was no really significant difference in rot resistance between the THPC-MM and the THPOH-MM samples. The THPC-NH_3 sample gave better rot resistance than the THPOH-NH_3 sample; however, it must be noted that the THPC solution was used in a precondensate form with urea, whereas, the THPOH was not.

One sateen sample treated with APO-THPC retained over 100-percent breaking strength after 3 months' soil burial, 67-percent after 4 months, and 40-percent after 5 months. One sample of THPC-MM treated sateen retained 76-percent strength after 3 months and 33-percent strength after 4 months. The duck treated samples were not as resistant as the sateen, but again APO-THPC and THPC-MM were the most resistant. The THPOH-MM sample retained only 18-percent after 3 months, but the weight increase was only 13-percent. At a higher add-on it would probably have been comparable to the THPC-MM sample. Among the treated sheeting samples, the THPC-MM had the best strength retention after soil burial. The sheeting samples—a lighter weight fabric— do not have as good resistance to micro-organism attack as the heavier fabrics, even at comparable add-ons. However, at 28-percent add-on, the sheeting has a better hand than the duck or the sateen.

The treated samples exhibiting the best rot resistance also afforded some protection against acid spotting and had improved dimensional stability. Thus, a limited reaction of the flameproofing polymer with the cellulose, although causing a loss of tensile strength, has the advantage of providing additional desirable properties, such as improvement in wrinkle recovery, dimensional stability, and acid resistance, as well as superior resistance to micro-organism with some degree of flame resistance still remaining.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Biagio Piccolo for phosphorus analyses and to members of the Textile Testing Investigations for physical properties.

REFERENCES

1. American Society for Testing Materials, 1954. ASTM Designation: (a) D1682-64; (b) D1295-60T; (c) D626-55T; (d) D737-46.

2. Beninate, J. V., Boylston, E. K., Drake, G. L., Jr., and Reeves, W. A. 1967. Better Flame Resistant Finish for Cottons. Textile Indus. 130 (11): 110, 112, 114, 116, 118.

3. Dean, J. D., Strickland, W. B., and Berard, W. N. 1945. The Soil Burial Test for Rot-Proofed Cotton Fabrics. Amer. Dyestuff Rptr. 34: 195-201.

4. Lawrence, E. W., and Phillips, R. H. 1956. "Wash and Wear" Fabrics. Amer. Dyestuff Rptr. 45: P548-P550, P561.

5. Perkins, R. M., Drake, G. L., Jr., and Reeves, W. A. 1966. Flame-Resistant Stretch. Textile Indus. 130(1): 125, 127-129, 164-165.

6. Reeves, W. A., McMillan, O. J., Jr., and Guthrie, J. D. 1953. Chemical and Physical Properties of Aminized Cotton. Textile Res. J. 23: 527-532.

7. Tripp, V. W., Piccolo, B., Mitcham, D., and O'Connor, R. T. 1964. X-Ray Fluorescence Analysis of Modified Cottons. Textile Res. J. 34: 773-777.

NOVEL FLUORINATED UREA FINISH FOR WATER AND OIL REPELLENCY

by

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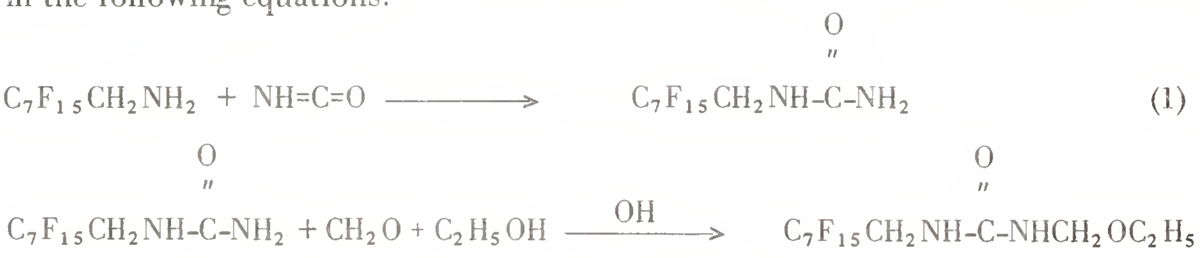
(Presented by W. J. Connick, Jr.)

INTRODUCTION

Fluorochemical fabric finishes have the unique ability to impart both oil and water repellency to textiles and are being widely used today on a variety of home furnishings and apparel fabrics. This paper reports a new fluorochemical finish, based on a fluorinated urea, which imparts oil and water repellency, as well as stain release properties, to cotton fabric.

RESULTS AND DISCUSSION

Several members of a novel class of polyfluorinated ureas have been prepared by reacting isocyanic acid (generated by the thermal depolymerization of cyanuric acid in a tube furnace at 390° C.) with fluorinated primary amines[1]. These monosubstituted ureas may be converted to the corresponding alkoxymethyl fluorinated ureas by a rather unusual base catalyzed reaction with formaldehyde and alcohols. A specific example is summarized in the following equations:



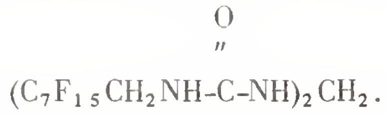
$$C_7F_{15}CH_2NH_2 + NH{=}C{=}O \longrightarrow C_7F_{15}CH_2NH\text{-}\overset{\overset{\large O}{\|}}{C}\text{-}NH_2 \qquad (1)$$

$$C_7F_{15}CH_2NH\text{-}\overset{\overset{\large O}{\|}}{C}\text{-}NH_2 + CH_2O + C_2H_5OH \xrightarrow{OH} C_7F_{15}CH_2NH\text{-}\overset{\overset{\large O}{\|}}{C}\text{-}NHCH_2OC_2H_5 \qquad (2)$$

I

The polyfluorinated ethoxymethyl urea, I, may be readily isolated in high yield.

Compound I may be applied to cotton fabric (pad-dry-cure) with an acid catalyst to impart high oil and moderate water repellency. Under acidic conditions, I forms the corresponding methylene bis-urea,



$$(C_7F_{15}CH_2NH\text{-}\overset{\overset{\large O}{\|}}{C}\text{-}NH)_2CH_2.$$

Formation of this highly insoluble compound probably is the basis for this finish. The finish may be applied from ethanolic solutions utilizing I which has been actually isolated or prepared in situ. Tests show that the first method gives the higher and more durable oil repellency.

A study of the catalyst requirements of this finish was made by comparing the oil repellency obtained without added catalyst and that obtained with either 1-

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[1] Ellzey, S. E., Jr., Wittman, J. S., III, and Connick, W. J. , Jr. Reduction of Polyfluoroalkyl Nitriles with Sodium Borohydride. J. Org. Chem. 30: 3945-3946. 1965.

percent $Zn(NO_3)_2.6H_2O$ or 3 percent $MgCl_2.6H_2O$. Initial oil ratings (AATCC) were identical under all conditions but after 15 home-type launderings, the uncatalyzed sample, while still having a fair degree of oil repellency, had a rating one or two units below either of the catalyzed samples. Slightly higher durability toward perchloroethylene extraction was obtained with $MgCl_2$.

Variation of curing temperatures (80°, 125°, 150°, 170° C.) did not appreciably affect initial oil repellency. Durability of extraction and laundering improved with cures of 125° and above.

Aqueous dispersions of I may be prepared by melting the compound at about 80° C, mixing it with a nonionic surfactant, adding boiling water, then stirring at high speed. The resulting dispersions are fairly viscous, but warming the padding bath to about 80° C. lowers the viscosity enough to allow easy application.

Samples of cotton print cloth (8 ft. x 18 in.) were treated with 1.25- and 2.5-percent ethanolic solutions of I, a combination solution of 1.25-percent I and 10-percent dimethylol dihydroxyethylenurea (DMDHEU), with a 2.0-percent aqueous dispersion. The catalyst for each was 3-percent $MgCl_2.6H_2O$. Samples were dried at 80° C. for 5 minutes and cured for 3 minutes at 155°. High initial oil ratings were obtained for all samples. Durability of oil repellency to 15 home laundry cycles was good for all four samples but poorest for the dispersion and the combination treatment. Best durability toward perchloroethylene extraction was obtained with the 1.25- and 2.5-percent solution. Water repellency (Spray Test) was initially in the range 70 to 80. After extraction (2 hr.) or laundering (15 cycles), all samples had a spray rating of 50. A high degree of wrinkle recovery was imparted by the combination treatment. Fabric color and hand were good for all samples. Tear strengths, breaking strengths, and flex-abrasion results are lower than for untreated control, as would be expected with the use of $MgCl_2$ at 155° C. The combination treatment was at least as good as a DMDHEU control in these properties. Moisture content and regain of the solution-applied I and the combination treatment were a little higher than for untreated control and much higher than for the DMDHEU control.

A stain-release test was devised where measured amounts of some common stains were applied to a fabric sample, evenly pressed in with a weight, blotted of any excess, then given one laundering along with other stained samples. Each sample was divided into squares and a different stain was placed in the center of each square. The stains were salad oil, black coffee, grape juice, motor oil, a suspension of carbon black in hexadecane, and mustard. A relative measure of the stain repellency could be obtained by a comparison of the samples after blotting but before laundering. Oily soil redeposition properties could be judged after laundering by noting any migration of carbon black to areas stained with oils. The finishes tested included compound I applied from an aqueous dispersion and ethanolic solutions, both alone and in combination with DMDHEU, and three commercial fluorochemical finishes (one of which was advertised as having "stain release" properties). Coffee and grape juice were effectively removed from all finishes. The urea derivative finish compared well with the commercial finish with "stain release;" neither showed oily soil redeposition. These were far superior to the other commercial finishes which showed heavy oil and carbon black stains and oily soil redeposition. Mustard was most easily removed from the urea derivative finish.

SUMMARY

An alkoxymethyl polyfluorinated urea imparts good stain-repellent and stain-release properties to cotton. This urea has been applied from ethanolic solution or aqueous dispersion and is compatible with a durable press reagent.

DISCUSSION

Question: Is the finish soluble in a chlorinated solvent?

Mr. Connick: The finishing agent has low solubility in these solvents.

RADIATION, WEATHER, AND ROT RESISTANCES OF SOME AROMATIC CELLULOSE DERIVATIVES

[SUMMARY]

by
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(Presented by T. Mares)

Energy absorbed by cellulose, whether from photochemical or high energy radiation, produced similar effects on the cellulose molecule; that is, activation of excited sites, oxidation, formation or reducing groups, depolymerization and evolution of gases. Because photochemical energies in the ultraviolet range involve only a few electron volts, energy absorption was found to be dependent on the molecular structure of the substrate and, therefore, was considered to be chemically specific. However, high energy, which involves several million electron volts, was not dependent on molecular structure and, therefore, was not chemically specific. The absorbed photochemical and high energies within the cellulose molecule, probably by intramolecular transfer, became localized in groups or bonds of the molecule, and produced similar chemical and physical changes in fiber properties. These changes resulted in chain cleavage and losses in the strength of cotton fibers.

Apart from cotton's susceptibility to radiation and weathering damage, cotton also is susceptible to attack by certain microorganisms. In the microbiological decomposition of cellulose, enzymes secreted by microorganisms attack the cellulose and induce hydrolysis; the products of hydrolysis are then utilized as food by microorganisms. Results of studies to improve cotton properties, with respect to degradation of cellulose by photochemical and high energy radiation, and microbiological attack, are presented in this report.

It was demonstrated that substitution of some aromatic groups on cellulose resulted in radioprotection, weather and rot resistances of cellulose. The radioprotection imparted to the cellulose molecule by benzoyl, cinnamoyl, and phenyl carbamoly ester groups, and benzhydryl and trityl ether groups extended over distances equivalent to several cellobiose units. Napthtoylation was moderately effective, but benzylation afforded little protection to cellulose from ionizing radiation.

Outdoor weathering data on cellulose benzoate, cinnamate, napthtoa benzhydryl and trityl celluloses indicated that only the benzoyl group imparted weather resistance to cellulose. After 26 weeks of outdoor weathering, the strength loss of unsubstituted cotton exceeded 70 percent; the strength loss of cellulose benzoate was only 10 to 20 percent.

Experimental data, on cellulose cinnamate and cellulose naphthoate, benzhydryl and trityl celluloses, showed that substitution of these aromatic groups on cellulose resulted in rot resistant cottons. After 2 weeks of soil burial, unsubstituted cotton retained no strength. After 30 weeks of soil burial, cellulose cinnamate retained 93 percent, benzhydryl cellulose 94 percent, and trityl cellulose 98 percent of their respective initial strengths. More impressive were results obtained by the naphthoylation of cellulose; cellulose naphthoate retained 89 percent strength, compared to that of the unsubstituted cotton, after 1 year of soil burial.

Protection of fibrous cotton cellulose from degradation by weathering, exposure to high energy radiation, and attack by microorganisms by substitution of suitable aromatic groups to cellulose was demonstrated. It can be concluded that in the protection of cellulose from degradation by weathering and high energy radiation, the presence of certain aromatic groups affected the absorption of incident energy by the cellulose or the localization of energy within the molecule or both. Also, it can be concluded that the nature of the linkage of the aromatic group to cellulose is not so important as the radiation stability of the linkage. Further protection of cellulose from microbiological degradation can be accomplished by substitution of some aromatic groups on cellulose, and this protection probably is caused by either the toxicity of these groups to microorganisms or to their inhibitory power toward microorganisms.

MILD CURE FINISHING PROCESS TO IMPART WET AND DRY WRINKLE RESISTANCE TO COTTON FABRICS

by
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(Presented by R. M. Reinhardt)

INTRODUCTION

There are four general classes of finishing processes for imparting wet and dry wrinkle resistance to cotton: (1) Conventional pad-dry-cure finishing, including deferred cure processing, (2) vapor phase or gaseous treatments, (3) wet treatments, and (4) moist cure or damp crosslinking processes. The latter class of finishing methods has been pioneered in Europe. Dry (or more properly, conditioned) wrinkle resistance is developed when certain critical conditions of treatment are met; namely, closely controlled moisture content during a relatively long reaction period.

The products of damp crosslinking have a number of properties that are desirable in finished cottons. Products with high dry wrinkle recovery and very high wet wrinkle recovery are produced. This combination is particularly important to give fabric with good smooth dry appearance when no tumble dryer is available and line drying is necessary.

A study of damp crosslinking was undertaken at this Laboratory and has led to the development of a simplified modification of the process that is more suitable to American finishing practice. Modifications have been made that permit elimination of the long treatment period of the European processes—usually 12 to 24 hours—during which moisture must be carefully controlled. Instead, a simple, mild cure treatment step has been substituted as the only processing operation necessary other than padding, washing, and drying.

The present paper discloses the new, mild cure finishing process and described the effects of the variables of the process. Variables include the nature and concentration of finishing agent and catalyst employed, the time and temperature of the mild cure processing step, and the interrelation of these factors with different fabrics and finishing equipment. Properties of the products are described and some comparison with those of conventionally finished cotton is provided. Also, the theoretical basis of the process from chemical and physical observations are considered. Additional details of the process and the products are being determined in continuation of this work.

EXPERIMENTAL AND RESULTS

Most experiments were carried out on 80 x 80 cotton print cloth with carbamate finishing agents. Dimethylol methyl carbamate (DMMC) was used to study the effect of processing variables.

No softener or other auxiliary agent was used in the treatments.

Standard test methods and analytical procedures were employed to characterize the finished cotton.

The mild cure finishing process consists essentially of the following steps:

(1) Impregnating the fabric with an aqueous solution containing a cellulose crosslinking agent and a strong mineral acid catalyst.

(2) Heating the impregnated fabric under mild conditions for a relatively short time without prior drying.

(3) Neutralizing and washing the treated fabric.

(4) Drying the washed fabric.

The treatment appears to be amenable to continuous processing. However, it has been carried out in batch steps on a laboratory and a semi-pilot plant scale. In the pilot plant, for example, cotton print cloth was padded to approximately 80 percent wet pickup with a solution containing 10-percent DMMC and 0.37-percent hydrogen chloride (1-percent hydrochloric acid), and cured on the tenter frame at 60° C. with a dwell time of 6 minutes and 40 seconds. The fabric had a moisture content of 4 to 5 percent after this treatment. After neutralization, washing, and drying, analysis of the treated fabric showed 0.64 percent nitrogen and 2.10 percent formaldehyde content. This indicates a molar ratio of HCHO/N of 1.53 in the treated fabric which is essentially equivalent to that generally found in fabric finished with the same agent in conventional pad-dry-cure treatments. Breaking strength of the treated fabric was 31 lb. which is 65 percent of that of the untreated. Conditioned wrinkle recovery was 265° (W+F); wet wrinkle recovery, 273°. Smooth dry ratings by the AATCC overhead lighting method after tumble-drying and line-drying were 4.3 and 4.7, respectively. These ratings are considerably higher than would be predicted from the wrinkle recovery values.

Results obtained in laboratory investigation of the variables of the process follow. In these experiments, the impregnated fabrics were placed on pin frames, cured in a forced-draft oven, then neutralized, washed, and dried.

Conditioned wrinkle recovery angles obtained upon heating print-cloth impregnated with a solution of 10-percent DMMC and 0.37-percent hydrogen chloride for various times at 40°, 60°, and 80° C. were determined. Development of improved wrinkle resistance correlated with loss of moisture and approach of the asymptotic moisture content characteristic of the treatment temperature. Further, the level of wrinkle resistance attained appeared to be related to the moisture content of the fabric. That is, high moisture contents during the mild cure treatment step inhibit the development of high levels of conditioned wrinkle resistance. This relationship is similar to that reported for the European damp crosslinking process. However, in the present process, the moisture level need not be maintained for such extended periods as in the European process.

Strength of the treated fabric varied as a function of the time of the cure. Thus, there is a point at which there is no further improvement in wrinkle resistance, but which is followed by progressive loss of strength. Therefore, an optimum relationship between strength and wrinkle resistance is achieved at the point at which the wrinkle resistance values level off. At 80° C., this point was observed at about 5 minutes' curing time; at 60° at about 7 minutes', and at 40° at more than fifteen minutes curing time.

The time-temperature curing relationship is altered for fabrics of other weights and structures and for other curing equipment. In addition to printcloth, treatment of sateen, oxford, and twill has been investigated.

Correlation of the drying curves, chemical analyses, and wrinkle recovery angles indicated that in mild cure finishing, reaction between DMMC and the cotton begins while the fabric is still wet. However, dry wrinkle resistance is not effectively improved until the moisture is reduced below about 5 percent.

The effect of catalyst concentration (0.1- to 3-percent hydrogen chloride) upon treatment of print cloth with 15-percent DMMC by the mild cure process was investigated. Samples were cured for 7 minutes at 60° C. with various concentrations of catalyst. Catalyst concentrations of 0.2 to 0.5 percent hydrogen chloride appeared to be optimum from strength and wrinkle recovery properties. For catalyst concentrations below about 0.8 percent hydrogen chloride, strength varied as a function of the level of wrinkle resistance of the fabric. With higher catalyst concentrations, greater losses of strength resulted with only small further increases in wrinkle resistance. Bound nitrogen content of the treated fabrics increased as a function of catalyst concentration. Wet and dry wrinkle resistance increased with catalyst up to about 2-percent hydrogen chloride concentration, above which slightly lower values were observed. Wet wrinkle resistanees were about 12° to 20° higher than conditioned recoveries for most treatments.

Other mineral acids could be employed as catalysts. Nitric and sulfuric acid provide effective catalysis at concentrations equivalent to those demonstrated with hydrogen chloride. Other acids, among them phosphoric, oxalic, citric, and tartaric, were tried as catalysts but were ineffective under the mild cure processing conditions.

Pad baths of 5 to 20 percent DMMC with 0.37 percent hydrogen chloride catalyst were used to study the influence of the concentration of crosslinking agent in the treatment. Curing was for 7 minutes at 60° C. The reaction efficiency of a conventional pad-dry-cure treatment is about 60 percent as calculated from the nitrogen content of the finished fabric. The reaction efficiency in the present case was also 60 percent, and it remained constant over the concentration range studied.

Improvement in wrinkle recovery is a function of crosslinking agent concentration but levels off with high concentrations. Wet wrinkle resistance levels off at higher concentrations than does dry wrinkle resistance. Tearing strength is decreased by the treatment but varies only slightly with concentration of agent used.

All of the common dimethylol carbamate agents were used in the mild cure finishing process. These included the dimethylol derivatives of methyl, ethyl, isopropyl, methoxyethyl, hydroxyethyl, and hydroxypropyl carbamate. All performed well. It should be noted that dimethylol hydroxyethyl carbamate, which generally requires stronger catalysis and reaction conditions than the other carbamate agents in pad-dry-cure finishing, functioned as well in the mild cure process as the more reactive homologues.

N-Methylol agents of other classes were investigated and many can be employed in the mild cure process. Effectiveness varies with the nature of the agent. In general, the order of effectiveness is approximately the reverse of the order of reactivity in conventional pad-dry-cure finishing.

Urea-formaldehyde cannot be used because it polymerizes in the presence of the strong catalyst. Dimethylol ethyleneurea and dimethylol propyleneurea give relatively poor results but may work better with further modification of the treatment conditions. Dimethoxymethyl uron and dimethylol dihydroxyethyleneurea can be employed successfully. A modified propyleneurea agent, dimethylol 4-methoxy, 5,5,-dimethyl propyleneurea, also gave good results.

It appears that agents that yield finishes that are resistant to acid hydrolysis perform better in the process than fast-reacting agents that give finishes that are not so acid-resistant.

Durable creases have been introduced into fabric finished by the mild cure process. The finished fabric was impregnated with a metal salt catalyst, such as zinc chloride or magnesium dihydrogen phosphate, and dried. It was then steam-pressed to shape and oven-cured as in the commercial post-cure process. This technique could provide another route to durable press garments. Further development of the creasing of mild cure finished cotton is being studied.

Fabric properties.—In general, the properties of fabrics processed by the mild cure finishing method are equivalent to those of fabrics finished by conventional pad-dry-cure treatment. Some of the properties are apparent from the preceding discussion.

High levels of wet and dry wrinkle resistance are produced which result in fabric that has high smooth dry ratings after tumble-, drip-, or line-drying. The relationship between strength and wrinkle resistance and the stress-strain relationship is about the same as in pad-dry-cure finishes. Similarly, abrasion resistance as measured by the Stoll flex test is about the same as in pad-dry-cure finishes. Resistance to chlorine damage is poorer in fabrics processed by mild cure finishing. Moisture regain of mild cure fabric is greater than that of pad-dry-cure fabric, but only by a small amount. The regain values are less than that of the untreated fabric. This indicates that the cellulose is crosslinked in a relatively tight matrix.

Electron micrographs were prepared from specimens of cotton fabric finished with DMMC by the mild cure process and by the pad-dry-cure process. The fabrics selected for this study had equal conditioned wrinkle recovery angles and nitrogen contents. Equivalence of the treatments at the microscopic level was demonstrated by study of the effects of layer expansion and cuene solubility techniques on ultra-thin sections. From microscopic studies it was concluded that a high degree of crosslinking is produced uniformly throughout the fiber by mild cure processing. Also, the mild cure conditions are sufficient to give a crosslinked structure equivalent to that produced by the more stringent conditions of conventional pad-dry-cure finishing.

Mechanism of reaction.—The crosslinking reaction in mild cure finishing is believed to proceed by a carbonium ion mechanism. Protonation of the methylol moiety of the finishing agent by the strongly acidic catalyst, followed by loss of water, yields the carbonium ion which is stabilized by resonance with an immonium ion structure. Reaction of cellulose with the carbonium ion gives a protonated cellulose intermediate which then loses the proton to yield the modified cellulose derivative. Similar reaction through the second methylol group gives the crosslinked cellulose.

Each step of the mechanism involves a reversible reaction. The rate determining step appears to be that in which water is eliminated as the leaving group from the protonated methylol compound to generate the carbonium ion. With the mineral acid catalyst used, the overall reaction apparently proceeds readily under the mild cure conditions. In pad-dry-cure finishing, catalysis is generally provided by a salt that is a Lewis acid rather than by protonation with mineral acid. Stronger curing conditions are required to affect reaction.

The apparent difference in reactivity of various agents in the two finishing processes also can be explained by this mechanism. In pad-dry-cure finishing, the Lewis acid salt catalysts provide weaker catalysis, and thus this type of finishing works best with highly reactive agents. A high level of acid stability by the finish is not necessary since reversal of the crosslinking reaction requires the presence of water. Water is not available as it is driven from the fabric at the high temperatures of curing.

In mild cure finishing, the strong catalysis and partial removal of water drives the reaction forward even with relatively less-reactive agents. However, only linkages that are highly acid resistant can survive because of the presence of the acid and moisture in the fabric during the treatment.

SUMMARY AND CONCLUSIONS

A process that employs a simple, mild cure treatment step has been developed for finishing cotton to impart high levels of wet and dry wrinkle resistance. Cotton fabrics of several weights and structures have been treated by the process to yield textiles that dry smoothly after either tumble-, drip-, or line-drying. Creases can be introduced into the finished fabric by a subsequent metal salt catalyst treatment.

The effects of the variables of the mild cure finishing process—principally the nature and concentration of the crosslinking agent and catalyst employed, and the time and temperature of the cure—have been determined and their interrelation indicated. Not all of the usual crosslinking agents are applicable in this process. Dimethylol carbamate agents are particularly suitable. Hydrogen chloride (from hydrochloric acid) provides effective catalysis under the mild curing conditions employed. Treatment conditions must be modified for fabrics of different weights and structures, and for different processing equipment.

The properties of cotton finished by the mild cure process are essentially equivalent to those of fabric treated by conventional pad-dry-cure treatment. The principal exception to this generalization is a higher level of wet wrinkle resistance in conjunction with high dry wrinkle resistance. This extra measure of wet wrinkle resistance produces a considerable increase in smooth drying performance after drip- or line-drying as compared with fabrics from conventional finishing. The latter generally merit high smooth dry ratings upon tumble drying but are less satisfactory when dried by other methods.

The crosslinking reaction in mild cure finishing is believed to proceed by a carbonium ion mechanism following protonation of the methylol moiety of the crosslinking agent by the strongly acidic catalysts used. Apparently this mechanism is operative with relatively moderate curing conditions and without the necessity of extensive dehydration of the fabric in the treatment. Chemical and physical evidence support the mechanism proposed.

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The authors wish to acknowledge the assistance of the following colleagues who have aided in the study: John S. Mason and Ann Black, for chemical analyses; Marilyn M. Smith, Constance F. Cashen, Mary F. St. Cyr, and others of the Textile Testing group for some of the tests; and Jarrell H. Carra for the electron microscopy.

DISCUSSION

Question: Does deferred curing cause a change in balance between wet and dry wrinkle recovery angle in comparing moist cure with pad-dry-cure? Is durability to laundering the same as in the pad-dry-cure process?

Mr. Reinhardt: The creasing work has just begun and I cannot give a definite answer. There is a slight change in wrinkle recovery angle. No extensive work has been done on durability at this stage, however, one would expect durability to be comparable to the pad-dry-cure process as chemical links are the same.

Question: What moisture conditions exist in the fabric after curing?

Mr. Reinhardt: Five to 6 percent moisture remain after curing.

Comment: A very similar process has been used for the past 2 years in Sweden. The conditions expressed by Mr. Reinhardt, namely, 7 minutes at 60° C. would be difficult to use in industry. The process in Sweden is particularly effective on broadcloth used in making men's shirts. The finished shirts withstand very high washing temperatures, 185° F. (85° C.), and have very good smooth drying properties even after spinning damp dry.

Question: Has any industrial scale production of the described work been accomplished? Can American finishers accomplish such a slow process? Wouldn't a one-half minute cure be more desirable and adaptable for commercial uses?

Mr. Reinhardt: As far as is known, no industrial scale applications have been attempted. More difficulty would exist in controlling conditions of cure by cutting time and raising the temperature.

Comment: The moist process is difficult to control.

Question (to Dr. Kärrholm): What conditions are used in Sweden?

Dr. Kärrholm: Higher temperatures are used, around 100° C., but more importantly, after curing the fabric should have 3-to 5-percent moisture regain. The moisture is difficult to control and causes trouble, varying also with fabrics being finished. It is being tried on bed sheets.

Question (to Dr. Kärrholm): How does the European housewife manage to achieve such high temperatures, 186° F. during washing?

Dr. Kärrholm: The machines include an independent electrical heater to raise the temperature of the wash water.

Question (to Dr. Kärrholm): Are results reproducible?

Dr. Kärrholm: Laboratory results are very good. Experiments are run many times and are expected to be better than within 10 percent, a suggested figure.

Question: Would the fabric be tendered if run at 80° C. for 5 minutes or if the tenter stopped during curing?

Mr. Reinhardt: Tendering may occur.

Dr. Kärrholm (when asked to comment further): We have not used carbamates, but DMDHEU is used. DMDHEU is very good, as good as in pad-dry-cure processes. No corrosion occurs as most equipment is made of stainless steel.

Question: What about chlorine retention and damage with the process?

Mr. Reinhardt: Resistance was not quite so good as in the conventional pad-dry-cure treatment.

PRE-CURE DURABLE PRESS FINISH THROUGH THE USE OF POLYMER DEPOSITION

by

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Southern Utilization Research and Development Division

(Presented by A. S. Cooper, Jr.)

A promising approach for developing satisfactory durable press finishes for all-cotton textile products involves some means of limiting the extent of crosslinking in combination with deposition of polymeric materials or within the cotton fibers or both. The Poly-Set Process is an example of such processes. As previously reported[1], this process involves two pad-dry-cure steps. In the first step, N-methylol crosslinking agents are deposited on and within the cotton fibers primarily by polymer formation using weak acid polymerization catalysts. Step two uses a strong latent acid catalyst to cause further crosslinking to obtain the desired smooth drying performance. The process is suitable for pre- and post-curing operations. Fabrics washed after the first step and impregnated with the crosslinking catalyst release very little formaldehyde or other disagreeable odors. At this stage, the fabric can be either cured immediately or stored for subsequent garment manufacture, creasing, and then delayed curing.

Zinc and zirconium acetates are effective polymerization catalysts for step one. The weak catalytic conditions in step one are sufficient to promote extensive reaction of the N-methylol compounds to form insoluble polymers, but apparently they are insufficient to cause extensive crosslinking reactions with the cotton cellulose as determined by changes in physical properties including wrinkle recovery angles. The use of zinc acetate as polymerization catalyst results in somewhat higher step one wrinkle recoveries than does zirconium acetate indicating a greater amount of initial crosslinking. This results in less sharp creases in garments for post-curing operations. For sharper creases zirconium acetate is the preferred catalyst. Of the N-methylol crosslinking agents, trimethylolmelamine (TMM) and a modified methylolmelamine (MMM) have the highest efficiency of polymer deposition. The carbamates appear to have the lowest efficiency in the Poly-Set Process. Curing conditions of about 3 minutes at 320° F. seem to be most desirable for step one. In step two of the process, zinc nitrate and magnesium chloride are effective catalysts and require about 3 to 5 minutes at 320° for curing of single layer fabric.

Breaking and tearing strengths of the Poly-Set processed fabric are somewhat greater than in fabric treated conventionally. The greatest improvement is in abrasion resistance which is generally several times that of the conventionally processed sample. The Poly-Set process is responsive to lubricant and softener additives in both steps. A polyethylene-polypropylene softener greatly enhances the wrinkle recovery when it is used in either or both step one and step two. These effects are durable to laundering in a home-type washing machine followed by tumble drying.

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[1] Reeves, W. A., Hamalainen C., St. Mard, H. H., and Cooper, A. S., Jr. Poly-Set Process for Producing Durable Press Cotton Goods. Textile Res. Jour. 37: 76-88. 1967.

The use of polymeric additives, such as polyurethanes[2], polyethers[3], and polyacrylates[4], with zinc acetate as polymerization catalyst results in high wrinkle recovery in step one. A resin combination of equal parts by weight of a modified methylolmelamine (MMM) and dimethylolpropyleneurea (DMPU) has been found to be particularly effective when zinc acetate is used as the catalyst and polyurethane as the polymeric additive in the first step of the Poly-Set treatment. The application of this first-step treatment to broadcloth and sheeting indicates that approximately 65 percent filling breaking strength and excellent abrasion resistance can be retained with wrinkle recovery angles up to 300°. Smooth drying performance ratings by overhead light are in the acceptable range for shirts and sheets. However, more extensive crosslinking can be promoted in one step by using zinc acetate as the polymerization catalyst together with small amounts of conventional crosslinking catalyst such as zinc nitrate or magnesium chloride. Zinc acetate catalyst alone does not produce as high smooth drying performance as the zinc nitrate catalyst. Adding the 1-percent zinc nitrate in combination with 2-percent zinc acetate causes a small reduction in flex abrasion resistance and strength properties and an increase in wrinkle recovery and smooth drying performance. Varying the concentration of zinc nitrate from 1 percent down to 0.25 percent causes progressive increase in flex abrasion resistance and strength properties and a reduction in smooth drying performance rating with not much change in wrinkle recovery angles.

Sheeting was treated with the resin combination (MMM-DMPU) in which both 5-percent zinc acetate and a mixture of 2-percent zinc acetate with 0.5-percent zinc nitrate were used as catalysts and including polyurethane and polyolefin in the formulations. For both catalysts the addition of polyurethane caused an increase in flex abrasion resistance, higher breaking strength, slightly lower tearing strength, and higher wrinkle recovery angles that was particularly evident in wet wrinkle recovery angles. The addition of polyurethane did not improve the wash-wear rating. Use of zinc acetate-zinc nitrate mixed catalyst produced a small improvement in smooth drying performance in comparison with zinc acetate alone but at some sacrifice in physical properties. The durability of the treatments as judged by smooth dry ratings seems about equal after 30 laundry-tumble dry cycles.

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[2] Blanchard, E. J., Harper, R. J., Jr., Gautreaux, G. A., and Reid, J. D. Improved Abrasion Resistance of Durable-Press Cotton by Single-Step Polyurethane Treatment. Amer. Dyestuff Rptr. 57: 610. 1968.

[3] Bruno, J. S., Harper, R. J., Jr., and Reid, J. D. Imine-Terminated Polymers Improve Cotton Durable Press Products. Textile Bull. 94(7): 33-35, 38. 1968.

[4] Harper, R. J., Jr., Blanchard, E. J., and Reid, J. D. Acrylates Improve All-Cotton DP. Textile Indus. 131(5): 172, 174, 177, 181, 184, 186, 233, 234. 1967.

A composite sheet was made from panels of each of these fabrics and included with them was a panel of a commercially produced durable-press sheet from 50/50 blend of polyester and cotton. This composite sheet was washed and tumble-dried 35 times in usual home-type laundry equipment. A common household detergent with no added bleach or laundry sour was used. There were practically no observable differences in the smooth drying performance of the different panels. The panels from fabric modified by the addition of urethane to the formulation showed a significant amount of yellowing that would make this urethane unsuited for white goods. Subsequent additional washes including a hypochlorite bleach, resulted in further yellowing of the samples with the urethane additive, and also significant yellowing in the other treated cotton samples not containing the urethane. This indicates that different resin combinations will be needed to produce white fabrics that are suitable for sheets and shirts.

In summary, pre-cure durable press cotton broadcloth and sheeting fabrics have been produced using the first-step of the Poly-Set process which consists of pad-dry-cure. Best overall tensile, abrasion resistance and wash-wear ratings were obtained when about 2 percent of a polyolefin was added to a 10-percent DMPU-MMM resin formulation catalyzed by either zinc acetate alone or with zinc acetate-zinc nitrate mixed catalyst. The addition of polyurethane resulted in some yellowing after 35 wash cycles, and additional washes containing a chlorine bleach resulted in further yellowing. Samples without the urethane also yellowed somewhat after chlorine bleach. It is thought that by proper resin selection fabrics can be produced by this process that merit further evaluation in end-use products such as sheets and shirts.

DISCUSSION

Question: What chlorine retention values do you get with your products?

Mr. Cooper: In our system using mixed resins we get considerably less chlorine tendering than using the resins individually. We have observed several cases showing this resistance.

Comment: We have obtained the same results when using carbamates in resin mixtures.

FIFTH SESSION: B. Norwick, Beaunit Textiles Division, Beaunit Corp., New York, N. Y., Chairman

EFFECTS OF FIBER PROPERTIES AND SPINNING VARIABLES IN DRAFTING TENACITY DURING SPINNING

[SUMMARY]

by

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Investigation of drafting tenacity is becoming more steadily important in the picture of textile research, because of the need to improve processing and to know the relationships between fiber properties and drafting tenacity.

In processing cotton through different stages, it is subjected to different operations, among which is roller drafting. The control of the short fibers causes the trouble in any drafting process. Usually this control is achieved through a high degree of fiber contact which in turn is brought about by drafting tenacity. The action is comparable to that taking place in a yarn or rope when it is subjected to a tension. This drafting tenacity has several components which are common to any drafting system. Some of these are fiber length, roller setting, fiber entanglement, fiber friction, and roving twist at the apron systems.

In apron drafting, the roving is usually subjected to a predraft or break draft. This is followed by a final draft in the apron zone. The aprons pass the fibers forward as the speed of the back rolls up to a point which is very close to the nip of the front rolls, so that there is little room for the uncontrolled movement of the floating fibers. In these systems it is interesting to examine the effects in terms of drafting tenacity which take place in the apron zone, since that is the final stage before actual spinning. In this connection the factors important to the practical spinner have been investigated. These are total draft, break draft, speed of drafting, spacing of the aprons, fiber length, and although less important, hooked ends of the fibers originating at the card.

Drafting tenacity decreases as the total draft increases; that is, the force per fiber is not independent of the draft.

This explains why the control of the floating fiber fraction is more difficult as the draft increases. This decrease in the drafting tenacity would still be higher were it not for the aprons that exert an additional pressure on the roving that increases the fiber cohesion in this zone.

The effect of the break draft can be compared to that of a roving subjected to a pull. At the beginning, for the very low break drafts, there is an increase in the drafting tenacity up to a maximum where the fibers reach their highest degree of contact, to be followed by a release, as soon as fiber slippage starts. Further increases in the break draft are then translated into a corresponding decrease in fiber tenacity at the front or apron draft zone.

It has been assumed in drafting theories that the effect of speed had no effect on the coefficient of fiber friction. On the contrary, as the speed increases so does the drafting tenacity, especially for coarse yarns.

Different fiber length parameters were correlated with drafting tenacity. These parameters were the 2.5-percent span length and 50-percent span length, measured on the Digital Fibrograph, as well as the U.Q.L. and the M.F.L. obtained from the comb sorter instrument. Also, correlations were calculated for these parameters divided by the Micronaire reading to take fineness into account. For the measurements on the Digital Fibrograph, it was found that the best correlations correspond to the 2.5 percent span length, but the correlation was very poor for the 50 percent span length. This agrees with the results found on the comb sorter instrument where the U.Q.L. correlated better with drafting tenacity than the M.F.L. did. When the fiber length parameters were divided by the Micronaire reading, the results were reversed in their ranking for now the best correlations correspond to the ratios 50 percent span length/Micronaire and the M.F.L./Micronaire, thus showing that for length measurements representing the whole fiber length distribution the fiber fineness definitely has an influence.

Examination of the whole fiber length distribution found on the comb sorter instrument partly confirmed the above results and also showed that the length alone gives, on the whole, a better correlation than the fiber length parameters divided by the Micronaire.

In an attempt to correlate the tenacity of the spun yarn with drafting tenacity of the material, a curvilinear correlation between the drafting tenacity and the tenacity of the spun yarn was found. But a linear correlation was found when the yarn tenacity was plotted vs. the product drafting tenacity x Stelometer (1/8 in. gage) bundle strength, thus showing that the tenacity of the spun yarn has two components--one, the drafting tenacity and the other, the tenacity of the fiber to break.

When trying to establish optimum processing conditions at the spinning frame, a high drafting tenacity is necessary to keep the fiber together and thus maintain a proper control of the floating fiber fraction. However, an excessive force may also cause defects in the yarn, such as increased irregularity, crackers, or even undrafted roving.

Drafting tenacity is a property that should be measured at the laboratory on a routine basis and should complement other properties of the material, such as length and fineness. This is now possible through instruments already available on the market. Also, it would be desirable to find a method to measure the drafting tenacity of the raw cotton before processing and thus be able to make a quick selection of the material to be spun in a quicker way than now.

Drafting tenacity offers good prospects for the establishment of optimum spinning conditions, for selection of cottons, for the establishment of the twist to be imparted to the roving, and the requirements of roll pressure for a given cotton at the spinning frame.

THE RELATION OF FABRIC STRUCTURE TO THE DURABLE-PRESS PROPERTIES OF MEDIUMWEIGHT COTTON FABRICS

by
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Southern Utilization Research and Development Division
(Presented by G. J. Kyame)

INTRODUCTION

The role of fabric structure in the wear performance of all-cotton, durable-press fabrics was sought in earlier research [1]/ [2]/ conducted on summer-weight suiting fabrics woven from yarns made from Pima S-2 variety of cotton. Two hundred and eighty-eight experimental fabric structures were evaluated. Half of these were made from plied yarns and half from equivalent singles yarns. Two levels of yarn size, two levels of yarn twist, four weave types, and three levels each of warp and filling thread counts were investigated. Evaluation of the fabrics by repeated laundering revealed that their performance depended chiefly on fabric weave, fabric thread count, and the size and kind of yarn used. The limited number of parameter levels explored, however, precluded a clear understanding of the influence of these parameters on fabric performance. This paper presents the results of an expanded investigation wherein the number of levels of some parameters were increased to more clearly elucidate the results.

MATERIALS AND METHODS

Fifty-four mediumweight experimental fabrics were woven. These encompassed combinations of two weaves, two yarn sizes, three warp thread counts, and from three to six filling thread counts, the number being limited by fabric weaveability on the one hand, and aesthetic acceptability on the other. The organization chart, figure 1, lists the fabrics woven. Yarns for the fabrics were spun from a two-bale blend of 1-1/8 in. Middling, American Upland cotton of 4.6 Micronaire reading and 76-percent maturity. The warp yarns were 10/1 (60 tex) and 15/1 (40 tex) spun to 4.10 T.M. and sized with a 12 percent add-on of conventional starch sizing. The filling yarns were 10/1 and 15/1, spun to 3.60 T.M. Thirty-three of the fabrics were 3/2 regular twills and 21 were plain-woven.

[1]/ Kyame, G. J., Harper, R. J., Lofton, J. T., and Ruppenicker, G. F., Jr. Improved Durable Press through Fabric Structure and Polymer Treatment. Amer. Dyestuff Rptr. 57: P662-P667. 1968.

[2]/ Kyame, G. J., Lofton, J. T., and Ruppenicker, G. F., Jr. The Effect of Fabric Structure on Durable Press Performance. In Proc. Seventh Cotton Utilization Research Conference. U.S. Dept. Agr., Agr. Res. Serv. ARS 72-63, pp 54-59. 1967. Textile Bull. 94(6): 37-39. 1968.

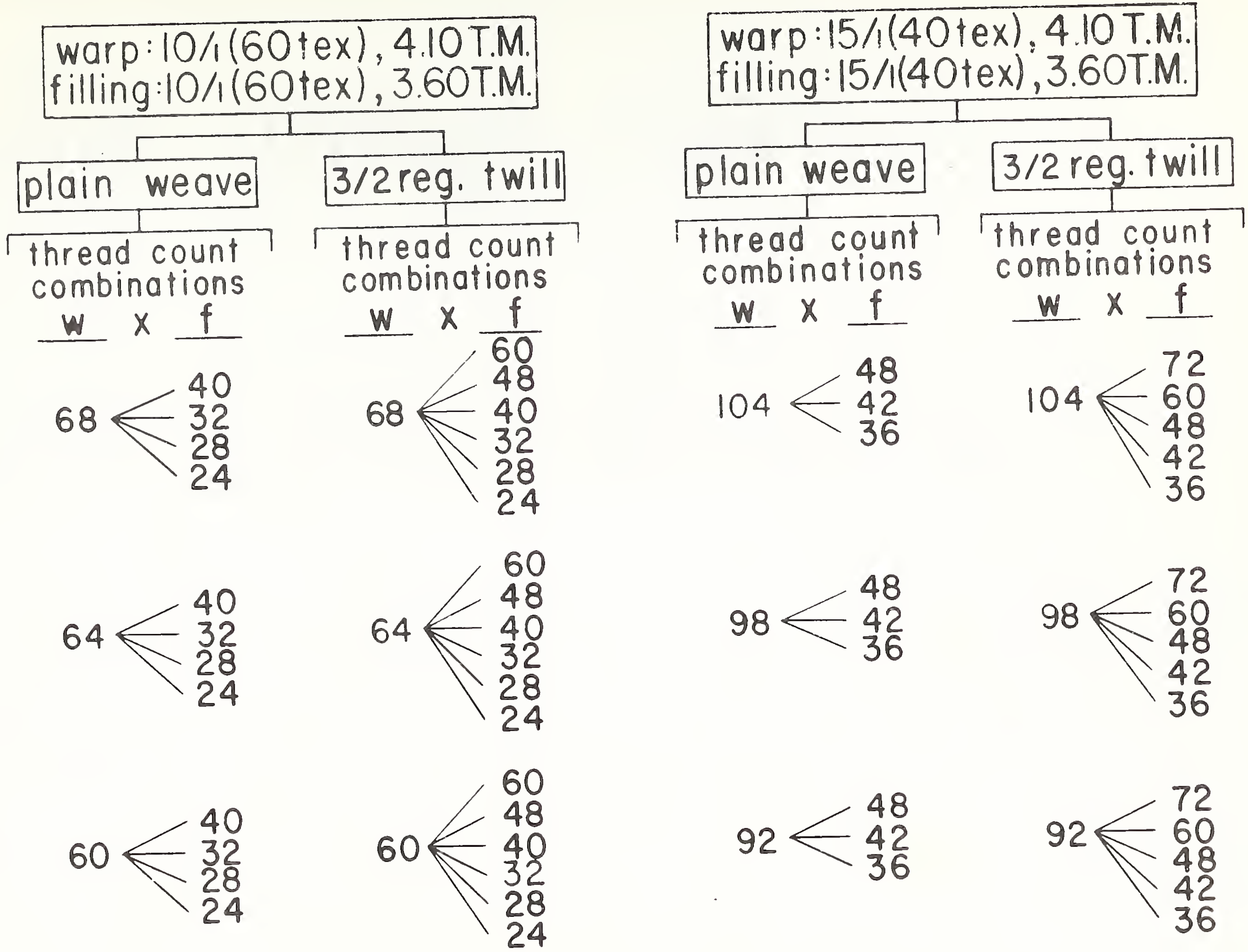
warp: 10/1 (60 tex), 4.10 T.M.
filling: 10/1 (60 tex), 3.60 T.M.
plain weave
3/2 reg. twill
thread count combinations
w x f
68
40
32
28
24
64
60
60
48
40
32
28
24
warp: 15/1 (40 tex), 4.10 T.M.
filling: 15/1 (40 tex), 3.60 T.M.
104
98
92
48
42
36
72
60
48
42
36

Figure 1.—Fabric organization chart.

Having determined the initial appearance ratings after the first laundering, the test trouser cuffs were given 29 additional launderings with inspections for damage after each cycle for the first five cycles. Subsequent inspections were made at cycles of 7th, 10th, 12th, 15th, and so forth. Fabric damage was classified under three categories: (1) Cycles to first failure (the breakage of a single thread), (2) cycles to first major damage (two or more crossings threads broken, or four or more paralled threads broken at the same site), and (3) the total number of holes after 30 launderings. This paper reports the findings under the first category, cycles to first failure.

RESULTS AND DISCUSSION

The susceptibility of mediumweight fabrics to early damage was clearly evident in the comparatively few launderings needed to cause fabric breakdown. This was particularly true of the plain-weave fabrics. Five of nine plain-wovens made from 15/1 yarn, and four of 12 made from 10/1 yarns failed between the fifth and seventh laundering cycles. This casts some doubt on the usefulness of these data for differentiating between the plain-woven fabrics, a fact that is given due consideration in the discussions that follow.

Statistical simple linear correlations were calculated to show relationships between fabric performance in repeated laundering and several of the fabrics' physical properties. These are given in table 1. In discussing the tabulated results, the correlation coefficients are categorized as follows:

Less than 0.60	poor
0.60-0.79	fair
0.80-0.85	good
0.86-0.95	very good
0.96-1.00	excellent

Correlations for the plain-weave fabrics are poor in most instances, no doubt the result of the fabrics' lack of durability to repeated launderings. Poor correlations are shown for all properties of the fabrics made from 15/1 yarns. The fabrics made from the 10/1 yarns, however, show a number of meaningful correlations. Fair correlations are indicated for warp tearing strength, filling breaking strength, bursting strength, flat abrasion, filling flex abrasion, filling stiffness, and resin add-on. The best correlation for these fabrics is the good -0.80 given for warp stiffness.

The twill weaves fare better. More than half the parameters treated were significantly correlated with laundering cycles to first hole formation. The degree of correlation ranged from fair (0.62) for the filling tearing strength of the fabrics made from 15/1 yarns, to a very good (0.89) for both the flat abrasion of the 15/1 yarn fabrics and the warp stiffness of the 10/1 yarn fabrics.

In an overall analysis wherein the data for all 54 fabrics were combined, only two parameters correlated significantly with laundering durability. These were filling tearing strength (good, 0.81) and resin add-on (fair, 0.67).

Table 1.—Simple correlation coefficients of fabric properties with average cycles to first failure.

Fabric Property	Correlation coefficients of—				
	Plain weave		Twill weave		Combined data
	10/1	15/1	10/1	15/1	
Tearing strength:					
Warp	0.73	-0.25	0.13	0.31	0.48
Filling	0.44	0.37	0.76	0.62	0.81
Breaking strength:					
Warp	0.22	-0.38	-0.30	-0.08	0.24
Filling	-0.76	-0.06	-0.85	-0.84	-0.49
Elongation-at-break:					
Warp	-0.55	-0.15	0.01	-0.78	-0.53
Filling	-0.28	0.31	-0.67	-0.87	0.20
Bursting strength	-0.64	0.12	-0.39	-0.81	-0.36
Flat abrasion	-0.65	-0.38	-0.77	-0.89	-0.37
Flex abrasion:					
Warp	-0.30	-0.45	-0.71	-0.74	-0.57
Filling	-0.63	-0.26	-0.76	-0.79	-0.56
Stiffness:					
Warp	-0.80	-0.31	-0.89	-0.85	-0.44
Filling	-0.70	-0.33	-0.85	-0.88	-0.45
Resin add-on	0.60	-0.25	0.72	0.03	0.67
Crease recovery angle:					
Conditioned	0.17	-0.46	0.14	0.02	-0.13
Wet	0.39	-0.36	0.58	0.57	0.41

Fifty-two additional experimental fabrics were prepared and evaluated for: (a) the effect of filling yarn size, (b) the effect of filling yarn twist, (c) the effect of variations in the plain and twill weaves, and (d) a study of sateen fabrics. A report on these supplementary studies is presented in a separate paper[3]

Finishing operations for all the fabrics included desizing, scouring, bleaching, and drying on a tenter frame under minimum tension settings. The bleached fabrics were given a conventional durable-press finish by padding on approximately 6 percent by weight of dimethylol dihydroxyelthylenurea (DMDHEU). The treated fabrics were dried on a tenter frame at 150° F. to a moisture content of about 9 percent.

One-yard samples of each of the treated fabrics were pressed flat in a steam-heated, hot-head, legger press, and cured for 8 minutes in a circulating hot air oven set for 320° F. The cured samples were given a single washing to remove unreacted resin and catalyst, then tumble-dried. Physical properties were then determined by standard ASTM test procedures.[4]

To determine fabric performance under repeated laundering, four 12 inch-long by 1-1/2 inch wide, cuffed, trouser legs were prepared from each of the sensitized experimental fabrics. These were creased, pressed, cured, and given a preliminary washing and tumble-drying. Wash-wear appearance and crease appearance were then rated substantially in accordance with AATCC test procedures.[5] Test standards were AATCC three-dimensional plastic replicas for rating wash-wear appearance, and AATCC Photographic Standards for rating crease appearance; both were used with overhead lighting.

All washing was done in 4-pound batches. Each batch was washed with 25 grams of Tide detergent in a Kenmore Model 600 washer operating through a normal cycle, that is, normal tub and agitator speeds, water temperature at about 105° F., 10-minute wash period, four rinses as follows: (1) spin-spray, (2) regular rinse, (3) deep rinse, and (4) spin spray, each of 2 minutes' duration, and a 4-minute spin-drying period. Tumble drying was carried out in an electrically heated, Kenmore Model 600 drier at a temperature of about 140° and a drying time of 45 minutes.

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[3] Ruppenicker, G. F., Jr., Kyame, F. J., and Little, H. W. The Influence of Yarn Parameters and Weaves on the Durable-Press Properties of Cotton Fabrics. Pages 111-122 of this Proceedings. 1969.

[4] American Society for Testing Materials. ASTM D1295-53T, D1682-59T, D1424-59, D1175-55T. 1966.

[5] American Association of Textile Chemists and Colorists. AATCC Tentative Methods 88A-1964T and 88C-1964T, Tech. Manual 41: B99-103, B104-105. 1965.

The indicated dependence of laundering durability on resin add-on is somewhat disturbing in that it implies a possible contribution of resin add-on to the variations in performance of the different fabric structures. However, the poor correlation with crease recovery angle, which is closely associated with resin add-on, minimizes this concern.

Numerous variance analyses of the data were made for all properties measured. Only those analyses that reveal relationships with fabric performance measured in terms of cycles to first failure will be discussed.

Fabric weave type plays a major role in determining a fabric's durability to laundering. This is demonstrated by the F-ratios given in table 2. Considering the 10/1 and 15/1 fabrics separately, the effect of weave is seen to be significant at the 99-percent probability level for both sets of fabrics. Filling thread count is also a major contributor to durability being significant at the 99-percent level for the 10/1 fabrics, and at the 95-percent level for the 15/1 fabrics. Interaction between filling thread count and weave type is significant at the 95-percent level for both sets of fabrics. Warp thread count, warp thread count-weave type interaction, and warp thread count-filling thread count interaction do not have a significant influence on durability-based F-ratios. In the overall analysis, the effects of weave and filling thread count on laundering durability are significant at the 99-percent level, and filling

Table 2.—Analysis of variance F-ratios—effect of weave on average cycles to first failure

Source of variation		10/1	15/1	Combined data
Weave	(W)	1/336.89	1/121.66	1/388.21
Filling thread count	(C_f)	1/ 20.03	2/ 14.16	1/ 25.44
C_f x W		2/ 7.51	2/ 10.71	2/ 11.39
Warp thread count	(C_w)	4.29	3.53	3.28
C_w x W		1.94	0.07	0.23
C_w x C_f		1.01	1.22	0.37

1/ Significant at the 99-percent probability level.

2/ Significant at the 95-percent probability level.

thread count-weave interaction is significant at the 95-percent level. No other significant effects are noted.

The importance of yarn size in determining fabric durability is demonstrated by the F-ratios in table 3. The effects of yarn number and of filling thread count are significant at the 99-percent level for the twill weave fabrics and in the overall analysis but are not significant for the plain-weave fabrics. The effect of warp thread count is significant at the 95-percent level for the twill fabrics only. None of the interactions was significant.

The significance of thread count in determining fabric durability is illustrated by the F-ratios in table 4. The filling thread count effect is significant at the 99-percent level in the 10/1 and 15/1 twill fabrics and in the overall analysis, and at the 95 percent level in the 10/1 plain-weave fabrics. Warp thread count was of significance in only the 15/1 twill fabrics (95-percent level). The general lack of statistically significant effects of warp thread count in this table and in tables 2 and 3 is believed due to using only three levels of warp thread count in the experiment.

The greater number of levels of filling thread count permitted a more detailed analysis of the effect of filling thread count on fabric performance. Preliminary plots of the data indicated a geometric relationship between the variables, so nonlinear regression models

Table 3.—Analysis of variance F-ratios—effect of yarn number on average cycles to first failure

Source of variation		Plain weave	Twill weave	Combined data
Yarn number	(Y)	0.62	1/104.85	1/67.48
Filling thread count	(C_f)	1.91	1/ 46.35	1/25.44
C_f x Y		0.83	1.61	0.69
Warp thread count	(C_w)	1.70	2/ 5.74	3.28
C_w x Y		0.10	2.20	0.91
C_w x C_f		0.16	0.49	0.37

1/ Significant at the 99-percent probability level.

2/ Significant at the 95-percent probability level.

Table 4.—Analysis of variance F-ratios—Effect of fabric thread count on average cycles to first failure

Source of variation	Plain weave		Twill weave		Combined data
	10/1	15/1	10/1	15/1	
Filling thread count	1/9.58	0.13	2/40.47	48.12	2/25.44
Warp thread count	1.97	1.31	7.08	1/ 5.11	3.28

1/ Significant at the 95-percent probability level.

2/ Significant at the 99-percent probability level.

were used. Figure 2 shows the least squares curve computed from the data for the 10/1 twill weave fabrics. Experimental data points are also plotted to show the scatter of the data about the calculated curve. The equation representing the curve is:

$$\log y = 3.76 - 1.56 \log x$$

where y = average cycles to first failure
x = filling thread count

The closeness of fit of the calculated curve to the experimental findings is evidenced by the relatively high correlation coefficient $r = -0.93$.

Superimposed on the figure are linear regression lines computed from associated data for fabric stiffness and crease recovery angle. Linear regressions were assumed in making these calculations. The influence of fabric stiffness on fabric performance is clearly evident. Increasing stiffness, whether in the warp or in the filling direction, produces a corresponding decrease in the number of laundering cycles required to cause fabric failure. A slight negative slope in the CRA line indicates increasing CRA with decreasing filling thread count. Normally, this would mean fewer cycles to failure for the fabrics with the lower thread count, but the tendency in this direction is far overshadowed by the predominant effect of fabric structure.

Figure 3 is a composite of figure 2 (fig. 3a), and three similar plots of the data for the 15/1 twills (fig. 3b), the 10/1 plain weaves (fig. 3c), and the 15/1 plain weaves (fig. 3d). The results in each case are similar, only the magnitudes differ. It is interesting to note the close similarity in the equations calculated for the twill fabrics:

(1) $\log y = 3.76 - 1.56 \log x$ (for the 10/1 twills)

(2) $\log y = 3.84 - 1.62 \log x$ (for the 15/1 twills)

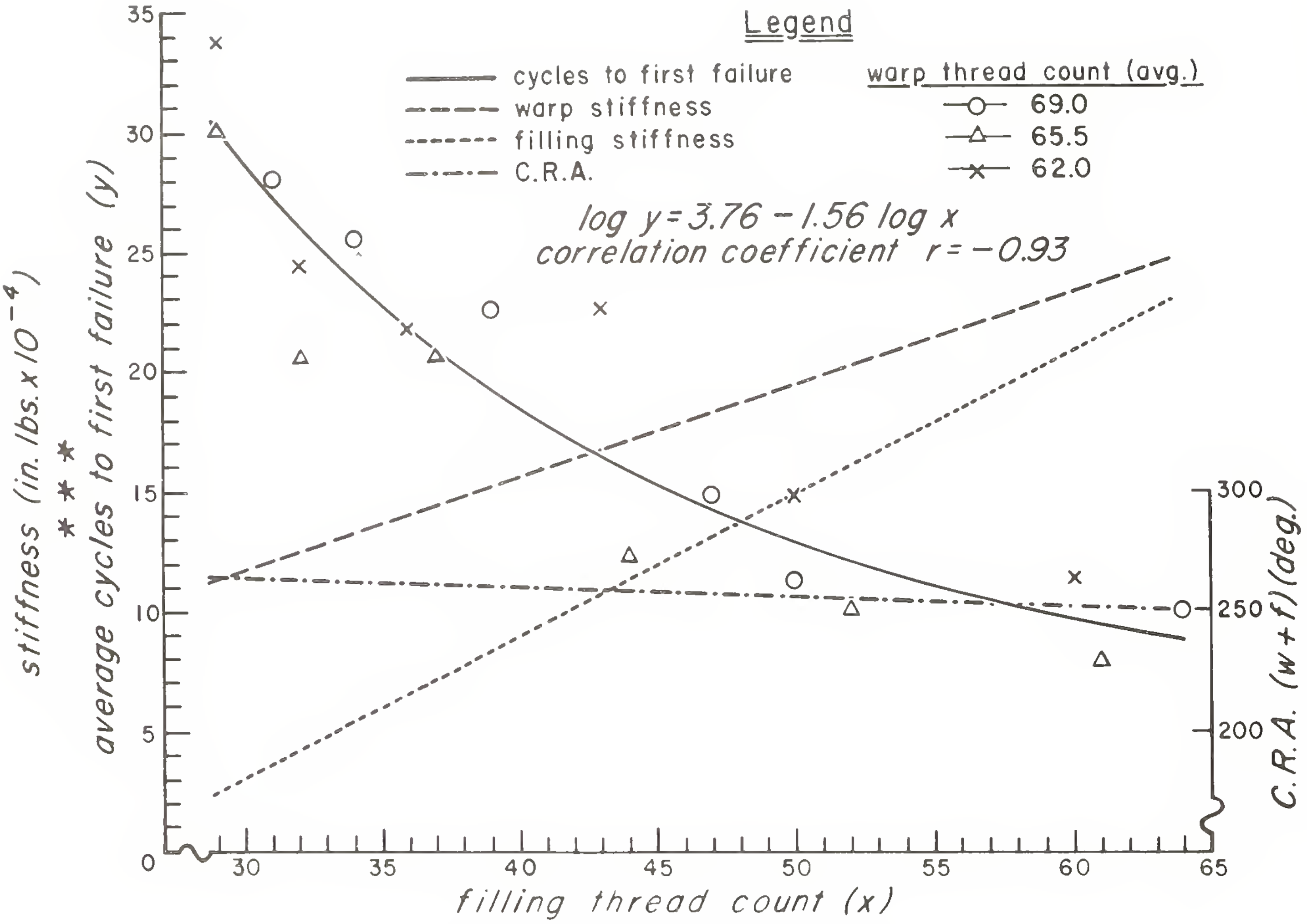
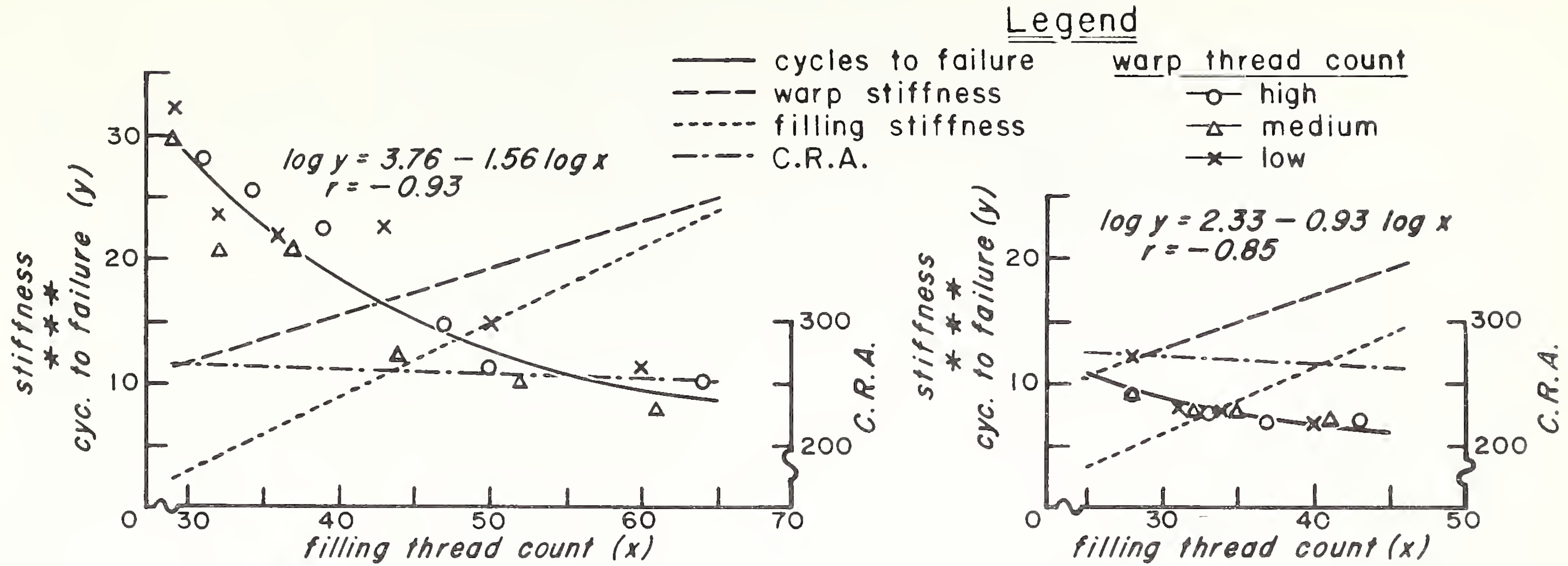


Figure 2.—Performance of the twills woven from 10/1 yarn.

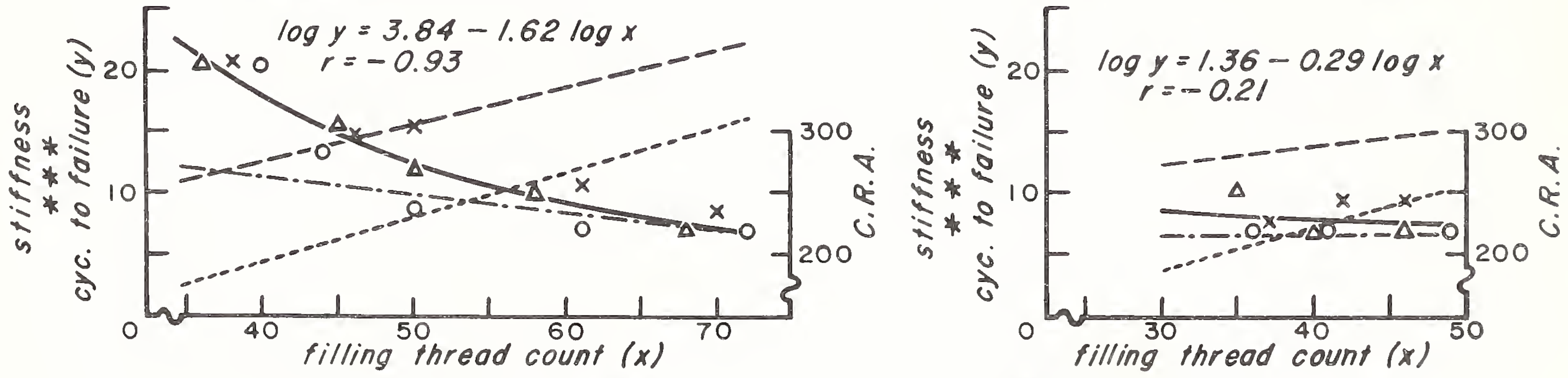
Rounding off the numerical quantities to the first decimal makes the equation identical. More research is needed to determine if this is meaningful.

Despite the poor performance of the plain weave fabrics, the effect of filling thread count is still clearly evident in figure 3c and figure 3d in that it again overrides the normal effect of CRA. Stiffness and crease recovery angle show relationships similar to those observed in the twill fabrics. In figure 3d, the comparative flatness and near horizontality of the performance curve is clearly the result of the breakdown of more than half the experimental fabrics by the seventh laundering cycle. The limited usefulness of this set of data is evidenced by the extremely poor correlation coefficient, r = -0.21.



(a). Twill weave, 10/1 yarn

(c). Plain weave, 10/1 yarn



(b). Twill weave, 15/1 yarn

(d). Plain weave, 15/1 yarn

Figure 3.—Performance of the experimental fabrics.

SEQUEL

The foregoing points up the enormity of the problem of relating the durable-press performance of a fabric and structural parameters of the fabric. The findings thus far allow only generalizations. It is clear that some weaves perform better than others; singles yarns outperform equivalent plied yarns in fabrics of the same kind and weight; and coarse yarns outperform fine yarns in equivalent fabric constructions. Much more research must be undertaken to determine the prerequisites for predicting a fabric's durable-press performance on the basis of its structural parameters. The Southern Division is continuing basic research along these lines.

ACKNOWLEDGMENTS

The authors deeply appreciate the participation of many coworkers in the Division's Cotton Mechanical Laboratory, Cotton Finishes Laboratory, and the Textile Testing Investigations in the preparation, finishing, and testing of many experimental fabrics. The financial support of the Cotton Producers Institute is greatfully acknowledged.

THE INFLUENCE OF YARN PARAMETERS AND WEAVES ON THE DURABLE-PRESS PROPERTIES OF COTTON FABRICS

by
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(Presented by G. F. Ruppenicker, Jr.)

ABSTRACT

The effects of weave, yarn size, and yarn twist on the durable-press properties of medium weight, all-cotton suiting fabrics are reported. Fabrics woven from several twill, plain, and sateen weaves were evaluated. Relationships between the home laundry performance of these fabrics and laboratory abrasion tests are discussed.

INTRODUCTION

The market for durable-press fabrics has experienced spectacular growth over the past few years. As a part of the Southern Regional Research Laboratory's overall research program to develop improved all-cotton durable-press products, investigations have been conducted to determine the effect of various yarn and fabric structure parameters on the properties of durable-press cotton fabrics.

Previous research determined at home laundry performance and other properties of light-weight durable-press suiting fabrics made from both single and plied cotton yarns. 1/ 2/ Generally, fabrics woven from singles yarns showed much better resistance to laundry wear than did those woven from plied yarns. Twill weaves provided the best resistance to wear, followed in order by sateens and plain weave fabrics. In most cases, an increase in thread count adversely affected wear because of laundering. Another study of heavier suiting fabrics woven from singles yarns produced similar results. 3/ The heavier weight fabrics wore much faster than the lighter weight fabrics.

This paper reports the effects of

1/ Kyame, G. J., Lofton, J. T., and Ruppenicker, G. F., Jr. The Effect of Fabric Structure on Durable Press Performance. In Proc. Seventh Cotton Utilization Research Conference. U.S. Dept. Agr., Agr. Res. Serv. ARS 72-63, pp. 54-59. 1967. Textile Bull. 94(6): 37-39. 1968.

2/ Kyame, G. J., Harper, R. J., Lofton, J. T., and Ruppenicker, G. F., Jr. Improved Durable Press through Fabric Structure and Polymer Treatment. Amer. Dyestuff Rptr. 57: P662-P667. 1968.

3/ Kyame, G. J., Ruppenicker, G. F., Jr., and Little, H. W. The Relation of Fabric Structure to the Durable-Press Properties of Mediumweight Cotton Fabrics. Pages 100-110 of this Proceedings. 1969.

weave, yarn size, and yarn twist on properties of mediumweight, all-cotton, durable-press, suiting fabrics. Fabrics woven from several twill weaves, variations of the plain weave, and some sateen constructions were evaluated. Relationships between the home laundry performance of these fabrics and laboratory flex abrasion tests are discussed.

MATERIALS AND METHODS

Yarns for the study were spun from a two-bale blend of 1-1/8 inch, Middling American Upland cotton with a Micronaire reading of 4.6. Fabrics ranging in weight from 7.50 to 9.00 oz./sq. yd. were woven from 10/1 and 15/1 warp yarns and from 7.5/1 to 15/1 filling yarns.

The fabrics were scoured, bleached, and treated with the following formulation containing an imidazolidone-type resin, Permafresh 183:

18-percent Permafresh 183
4-percent Velvetol OE (softener)
3.2-percent Catalyst X-4
Balance water

The resin solution was applied on a padder to a wet pick-up of approximately 65 percent and dried on a tenter at 150°F. to a moisture content of from 8 to 9 percent.

For determining the treated fabrics' durability to laundering, the sensitized fabrics were made into cuffed trouser legs measuring approximately 9-1/2 inches wide by 12 inches long. These were fabricated with the warp yarns running lengthwise. The cuffs were pressed on a steam-heated, automatic press on cotton setting and then cured in a hot air, circulating oven for 8 minutes at 320°F. Four cuffs were made from each fabric. Additional sets of cuffs were made from the twills and sateens with the backs of the fabrics exposed to the outside. All were washed and tumble dried a total of 30 times in standard home laundry equipment with a normal wash cycle, in accordance with AATCC procedure. 4/

The cuffs were checked after every second and fifth wash-dry cycle and the number of cycles to failure recorded. A single broken thread, either warp or filling, was considered a minor failure. A break in both warp and filling, or a break in four or more warp or filling yarns at the same site constituted a major failure. In some instances both minor and major failures occurred on the same wash cycle. Holes developing in the hemmed, upper edge of the test specimens were not counted. Crease damage was assessed separately.

After the first laundering and at

4/ American Association for Textile Chemists and Colorists. AATCC Tentative Methods 88A-1964T and 88C-1964T, Tech. Manual, 42:B102-106, B107-108. 1966.

the end of the evaluation, the cuffs were rated for wash-wear appearance and sharpness of creases. Rating procedures followed substantially those recommended by the AATCC. [4] The test standards were AATCC plastic replicas for rating wash-wear appearance, and AATCC photographic standards for rating crease appearance.

Abrasion resistance and other physical properties were measured on samples of the fabrics pressed flat, cured, and laundered once to remove unreacted resin and catalyst. The fabrics were tested in accordance with ASTM procedures. [5]

RESULTS AND DISCUSSIONS

Generally, all the fabrics had excellent durable-press properties. The fabric treatment resulted in an average resin add-on of about 5.7 percent. Wash-wear and crease appearance ratings averaged 4.0 or better after both one and 30 launderings. The average

Table 1.—Properties of a sateen fabric before and after resin treatment

Property	Untreated [1]	Treated [2]	Decrease
			Pct.
Breaking strength (lb.):			
Warp	146	72	50.6
Filling	150	57	62.0
Tear strength (gr.):			
Warp	2,867	2,500	12.8
Filling	3,300	2,067	37.4
Flex abrasion (cycles):			
Warp	665	155	76.6
Filling	1,110	220	80.1

[1] Scoured and dyed fabric.

[2] 18-percent Permafresh 183.

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[5] American Society for Testing Materials. 1966. ASTM D1295-53T, D1682-59T, D1424-59, D1175-55T. 1966.

crease recovery angle (conditioned. warp + filling) was approximately 272°.

The resin-treated fabrics exhibited substantial decreases in strength and abrasion resistance. Table 1 shows the properties of a 9-oz. warp sateen fabric before and after resin treatment. Breaking strength decreased 50-percent warpwise and over 60-percent fillingwise. Tear strength losses were somewhat less--approximately 13-percent warpwise but over 37 percent fillingwise. There were decreases in flex abrasion

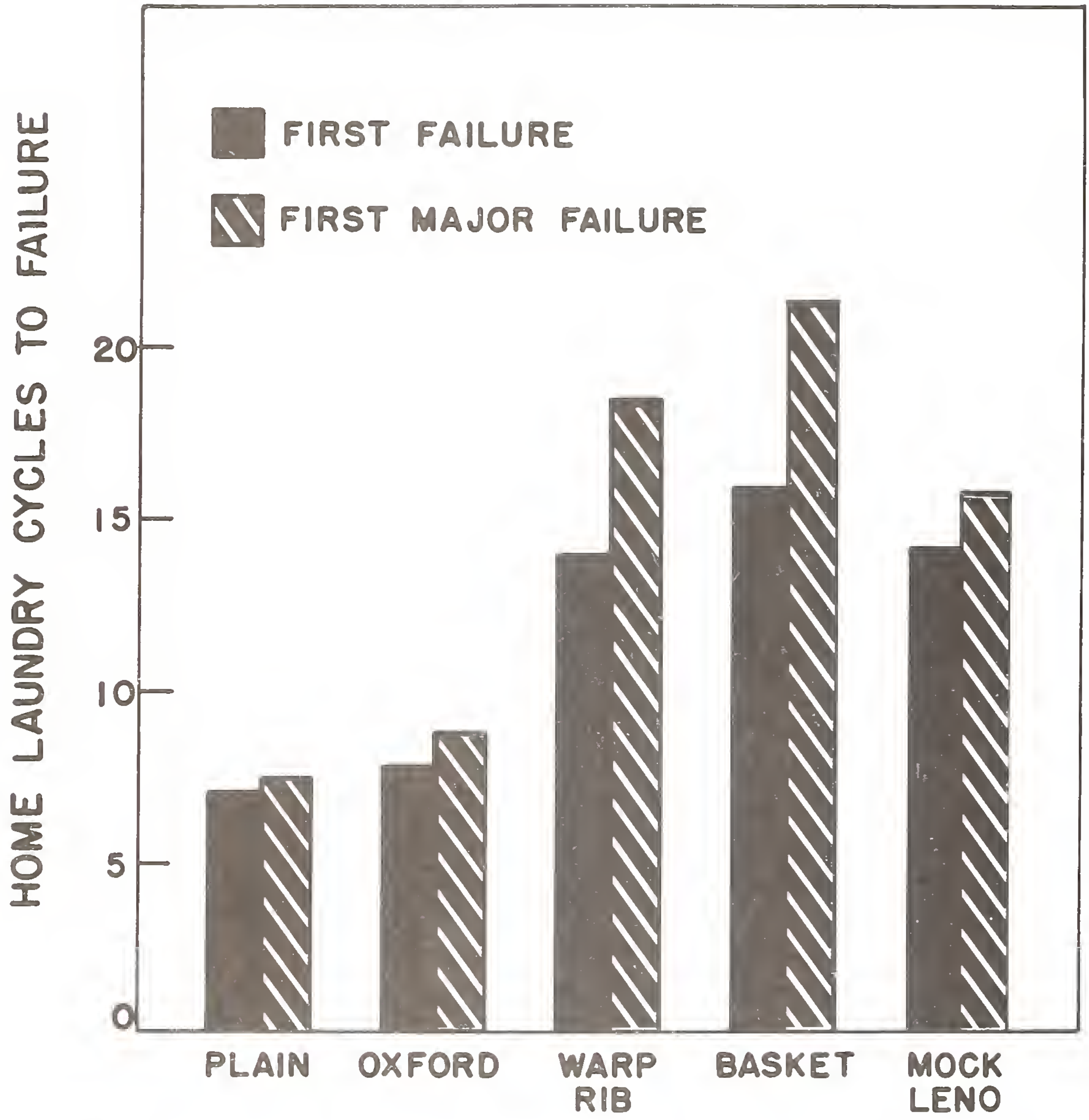

Figure 1.–Home laundry performance of plain weave type fabrics.

resistance of up to 80 percent compared with untreated fabric.

Plain weave and related fabrics—Plain weave fabrics are used extensively as suiting and trouser materials. Previous work has shown that all-cotton, durable-press, plain weave fabrics exhibit very poor wearing qualities in repeated home laundry tests. This is believed to be because of the high degree of yarn interlacings that restrict yarn movement and thereby make the fabric more susceptible to edge wear. In the present study, several plain weave derivatives including the oxford, 2/2 warp rib, and 2/2 basket were evaluated. Some fabrics woven with a six-harness mock leno weave were also included. Figure 1 shows the laundry performance of these fabrics compared with plain weave fabrics. The results are averages for 8 oz./sq. yd. fabrics woven from both 10/1 and 15/1 yarns. The average number of cycles to first failure and to first major failure are shown for each weave type. There was a very good correlation between the two levels of measurement. Most of the initial failures were warp yarns. All the derivative weaves performed better than the plain weave, with the basket weave fabrics having the best laundry durability. There was very little difference in wear between the oxford and plain weave fabrics. An examination of the cuffs after 30 launderings revealed that those woven from the plain weave fabrics also had extensive crease damage.

Figure 2 shows the flex abrasion resistance of plain weave fabrics. Flex abrasion was measured with a Stoll Universal Wear Tester. In this test, the fabrics are subjected to unidirectional rubbing and folding action as opposed to wear on a folded edge determined by laundry tests on the cuffed trouser leg specimens. The results for flex abrasion resistance were generally opposite to those for laundry performance. The plain and oxford weave fabrics had the best flex abrasion resistance, both warpwise and fillingwise.

Twill weave fabrics—Figure 3 shows the home laundry cycles to major failure for some twill weave fabrics comparable in weight and construction to the plain weave type fabrics already discussed. Cuffs for laundering were made with both the face and back sides exposed. Generally, the durability to home laundering increased as the length of the yarn floats increased. The 2/2 twill wore much better than the 2/1 twill. Very little difference in wear existed between the face and back sides of the fabrics. There was no apparent crease damage for any of the twill weave fabrics after 30 home laundry cycles.

The flex abrasion resistance of twill fabrics is shown in figure 4. The results were inconclusive. Fillingwise, abrasion resistance decreased as the length of the yarn floats increased. The 2/2 twills behaved approximately the same on both sides. There was a much greater difference between warpwise and fillingwise abrasion resistance on the back side than on the face side of the fabrics. In most cases, the highest values were obtained when the abrasive action was perpendicu-

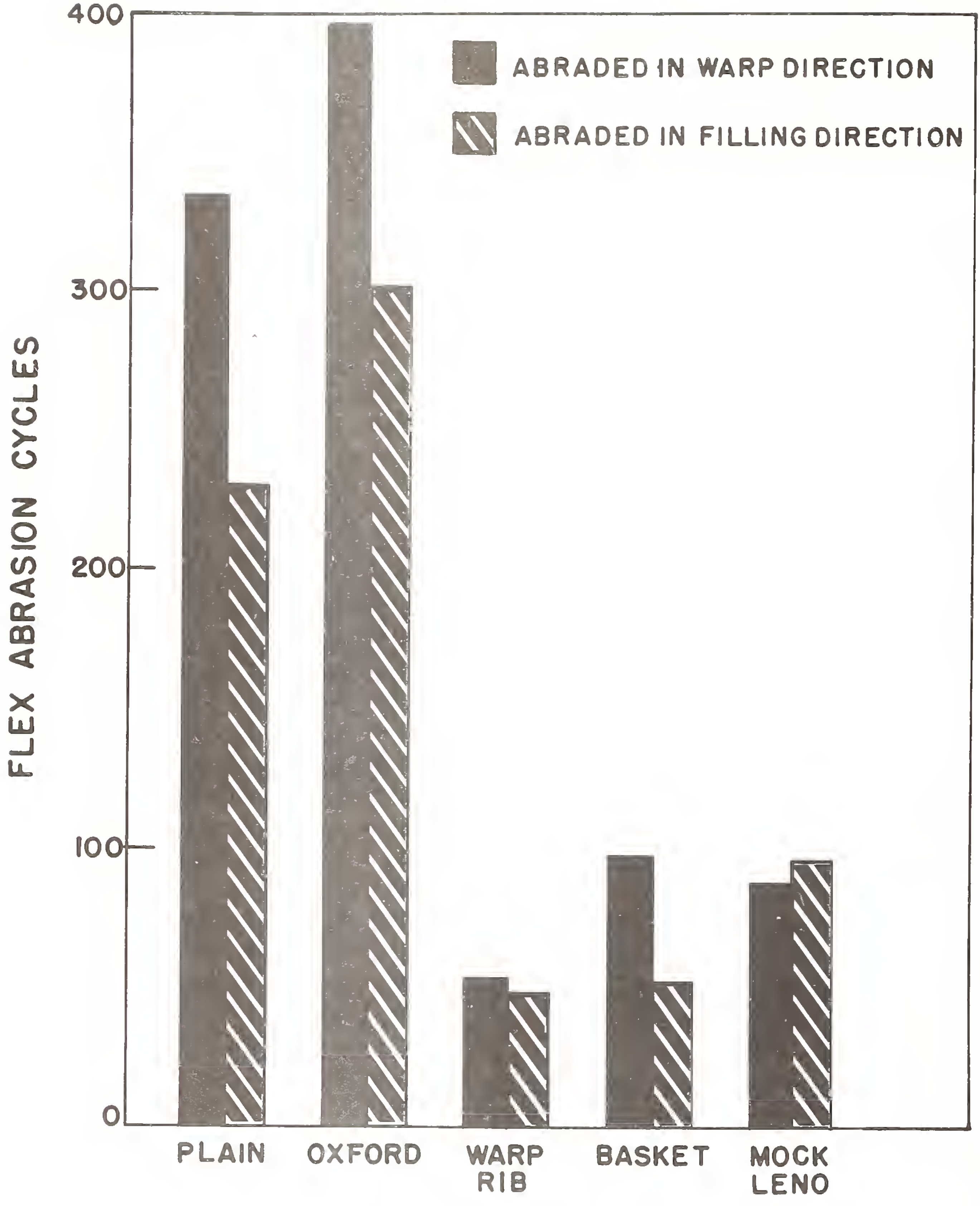

Figure 2.—Flex abrasion resistance of plain weave type fabrics.

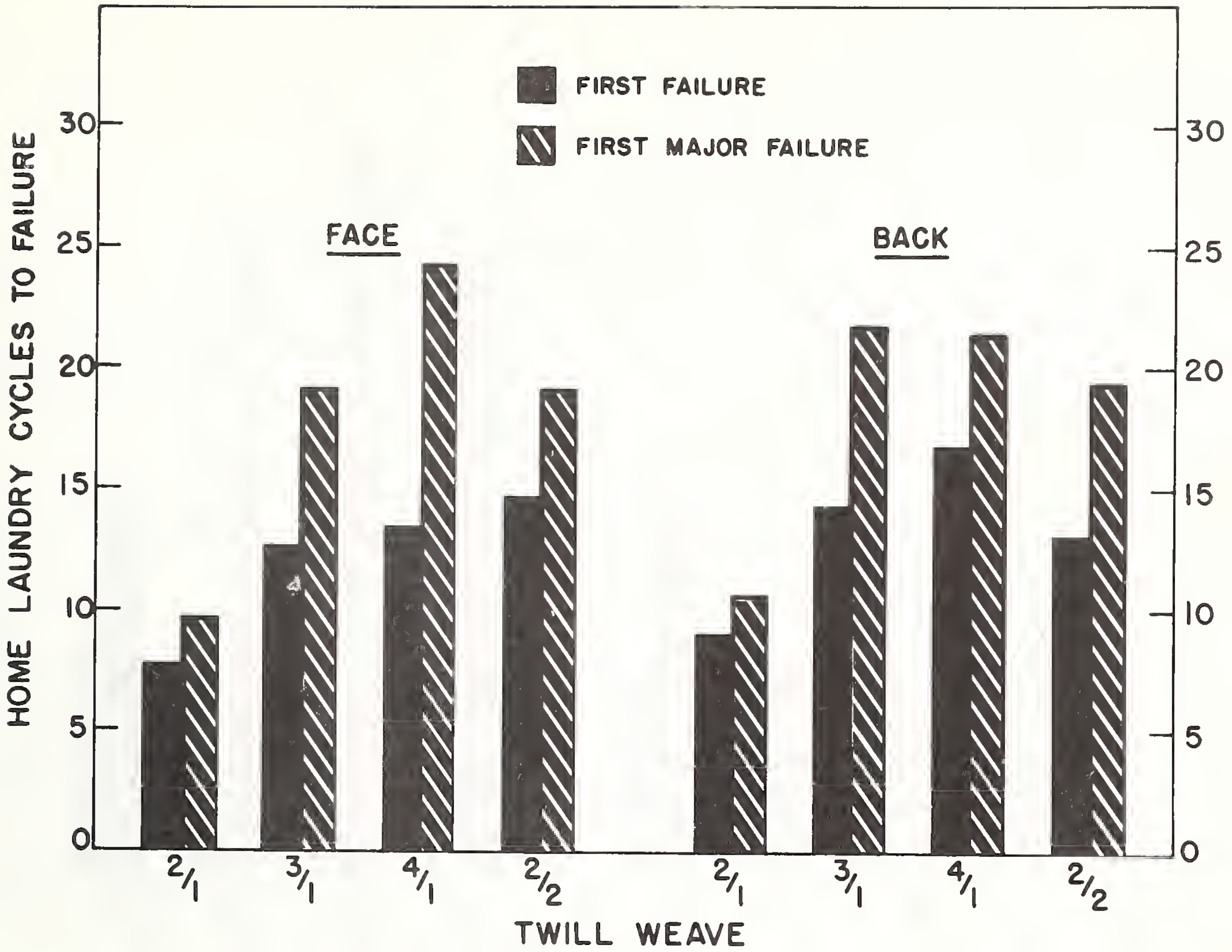

Figure 3.–Home laundry performance of twill weave fabrics.

lar to that of the predominantly exposed yarns.

Sateen fabrics–Figure 5 shows the effect of home laundering wear on cuffs made from three sateen fabrics, each weighing approximately 9 oz./sq. yd. One fabric was woven with 10/1 yarns, another with 15/1 yarns, and the third with 15/1 warp yarns and 10/1 filling yarns. These fabrics were laundered and tested with both the face and back sides exposed. The fabric woven with 10/1 warp and filling yarns withstood about twice as many laundry cycles as the others before showing major failure. Examination after 30 launderings showed some crease damage in the fabric woven from 15/1 yarns. There were no real differences in wear between the face and back sides of the fabrics. However, with the face exposed, initial failures were warp yarns, whereas with the back exposed, initial failures were filling yarns.

The fabric woven with 15/1 yarns in both the warp and filling had the best flex abrasion resistance. As with the twill fabrics, the highest values were obtained when the abrasive action was in

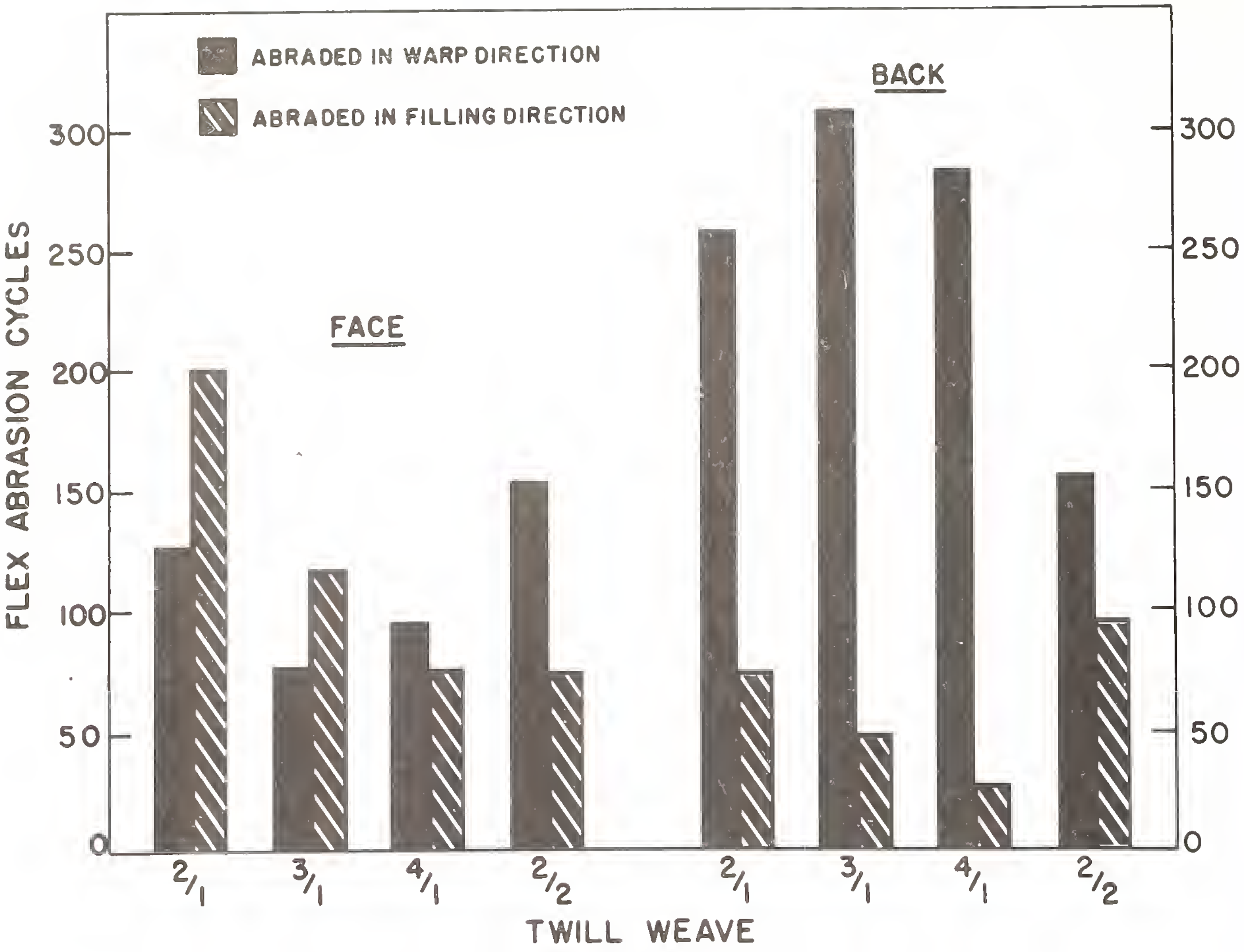

Figure 4.–Flex abrasion resistance of twill weave fabrics.

the opposite direction to that of the exposed floats. There were no significant differences in flex abrasion resistance between the face and back sides of the fabrics.

Effect of yarn number on wear–The effect of yarn number on home laundry performance is shown in figure 6. Plain and 3/2 twill weave fabrics weighing approximately 7.5 oz./sq.yd. were woven from 10/1 and 15/1 warp yarns and 7.5/1, 10/1, 12.5/1, and 15/1 filling yarns. Another series of 8 oz./sq.yd. fabrics was woven from the same yarns. Fabric weights in each series were held constant by adjusting the thread count to compensate for changes in yarn size. The results shown are the combined averages for the 7.5 and 8.0 oz./sq.yd. fabrics. Laundry performance improved with an increase in filling yarn size for both the plain and twill weaves. In contrast to the sateen fabrics shown in figure 5, warp yarn number had no significant effect on wear for this group of fabrics. However, it is possible that a greater range in warp yarn number may have shown some differences. The 3/2 twills withstood from two to three times more laundry wear than the plain weave fabrics. As already noted, the plain weave fabrics had extensive crease damage after 30 home laundry cycles.

Warpwise and fillingwise, flex abrasion resistance decreased as the filling yarn size was increased. Fabrics woven from both the 10/1 and 15/1 warp yarns showed the same trend. The plain weave fabrics were considerably better in this property than the twill fabrics.

Effect of yarn twist on wear—The laundry performance of 8 oz./sq.yd. fabrics woven from filling yarns spun with three different twist multipliers ranging from 3.10 to 4.10 is shown in figure 7. All warp yarns were spun with a 4.10 twist multiplier. The results shown are averages for fabrics woven from both 10/1 and 15/1 warp and filling yarns. Filling yarn twist had no significant effect on laundry wear for either the plain or twill weave fabrics. These results agree with the previous findings that neither warp nor filling yarn twist has a significant effect on laundry wear.[1]/[2]/ The twills wore much better than the plain weave fabrics. There was very little difference between cycles to first failure and cycles to first major failure for the plain weave fabrics, many of which failed both ways on the same laundry cycle.

Filling yarn twist had no significant effect on flex abrasion resistance. The plain weave fabrics were much better in this property than were the twills. Higher values were obtained when the fabrics were abraded in the warpwise rather than the fillingwise direction.

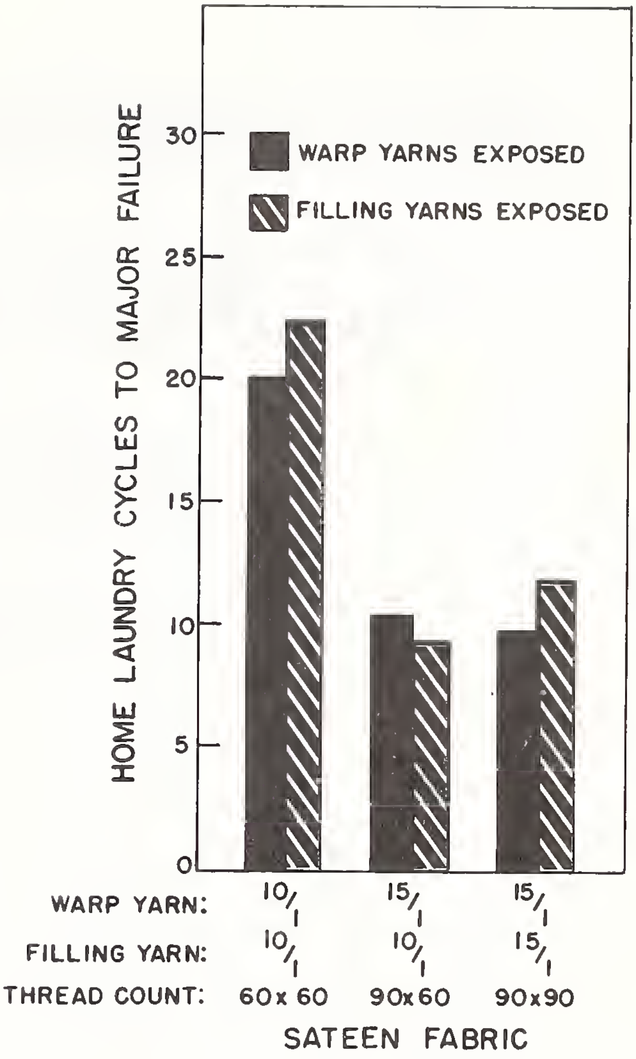

Figure 5.—Home laundry performance of sateen fabrics.

SUMMARY AND CONCLUSIONS

Differences in the laundering wear of the durable-press cotton fabrics investigated appear to be caused primarily by the effect of yarn mobility within the fabric structure. Plain weave fabrics exhibited poor laundry wear compared to the more flexible baskets, ribs, twills, and sateens. Fabrics woven from coarse filling

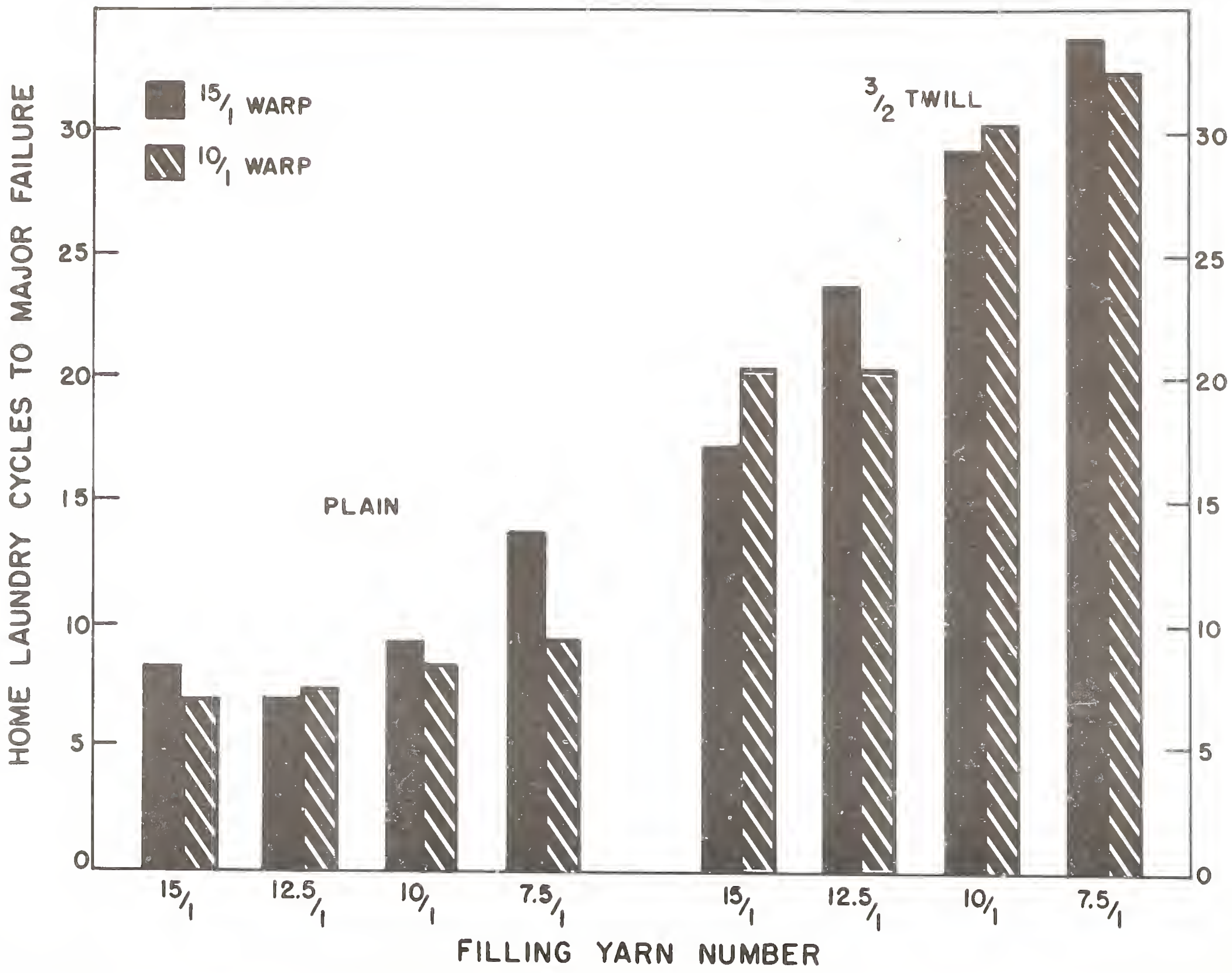

Figure 6.—Home laundry performance of fabrics woven from different yarn numbers.

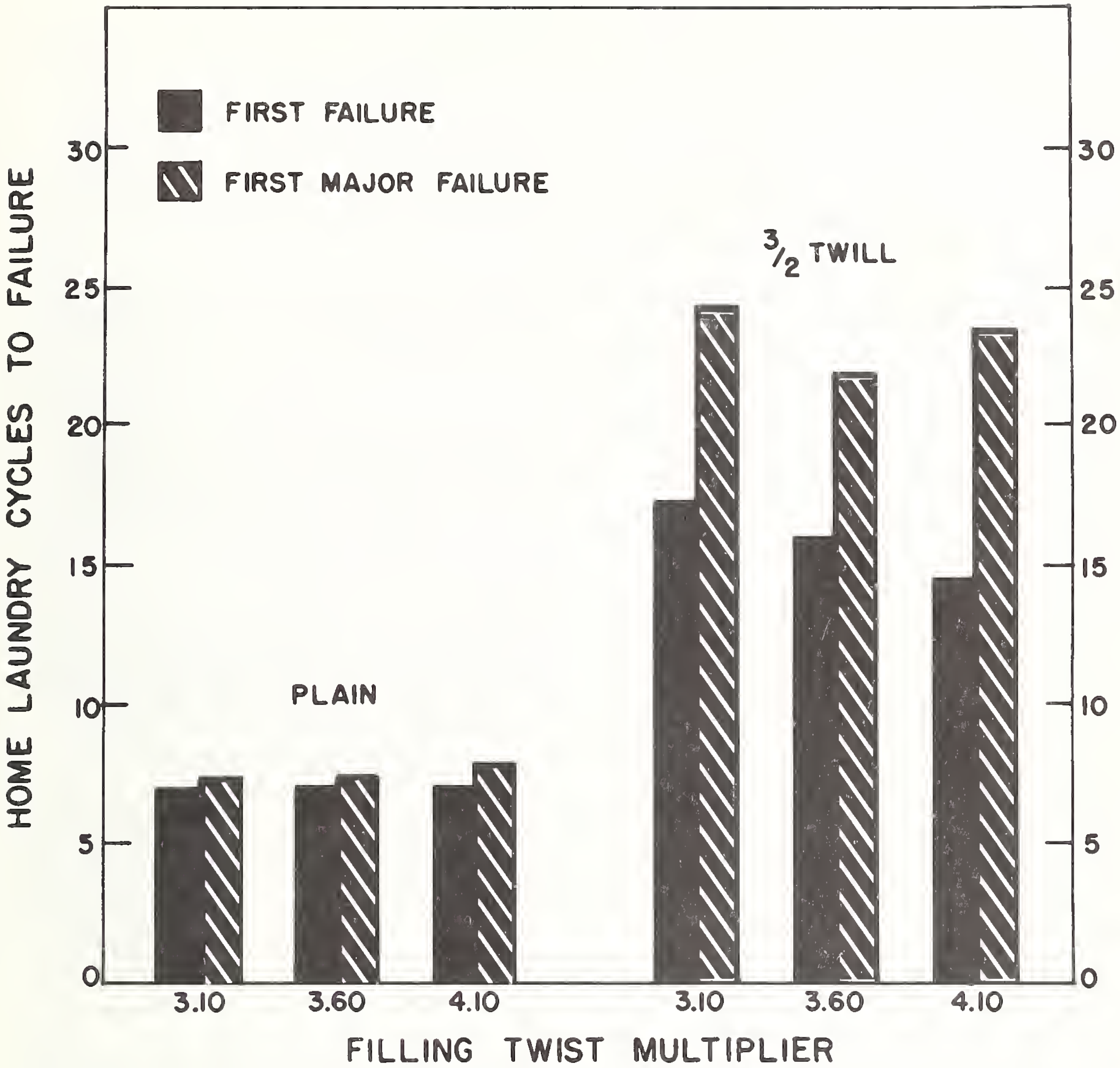

Figure 7.–Home laundry performance of fabrics woven from filling yarns having different twist multipliers.

yarns wore better than those of comparable weight woven from finer yarns. Yarn twist had no significant effect on fabric performance. Neither were there any real differences in wear between the face and back sides of the twill and sateen fabrics.

The results for flex abrasion resistance were, in most cases, opposite to those for laundering wear. The plain weave type fabrics had the best flex abrasion resistance, but the poorest laundry wear. Fabrics woven from finer yarns produced better flex results than those woven from coarse yarns. Filling yarn twist had no significant effect on flex abrasion resistance. Nor were there any real differences between the face and back sides of the twill and sateen fabrics in this property.

ACKNOWLEDGMENTS

The authors express their sincere appreciation to coworkers in the Division's Cotton Mechanical Laboratory, Cotton Finishes Laboratory, and the Textile Testing Investigations for their contributions in the preparation, finishing, and testing of the fabrics; and to G. I. Pittman for preparing the figures. They grately acknowledge the financial support of this study by the Cotton Producers Institute, and the cooperation of the National Cotton Council of America.

DISCUSSION

Question: What laundry conditions were used on the fabrics?

Mr. Ruppenicker: The fabrics were laundered in standard home laundry equipment with AATCC procedures, that is, 140° F. wash water initial temperature followed by tumble drying at 140° temperature.

Question: Should we put our condifence in a flex abrasion test or a laundry test?

Mr. Ruppenicker: Each test measured a different property in a fabric. Because cotton fabric wears first on edges and creases, we have put more emphasis on the laundry test.

Question: I'm also concerned about the inconsistency between laundry wear and flex abrasion. Wouldn't flat abrasion be a better measure of the type of wear associated with knee burst?

Mr. Ruppenicker: We have no information along these lines. However we have not obtained good correlation between either flex abrasion or flat abrasion and laundry wear tests.

Comment: ASTM is setting up a committee on laundry tests on durable press fabrics that will study the relationships between wear and fabric properties.

DURABLE PRESS COTTON FABRICS WOVEN FROM POLYMER SIZED YARNS

by
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(Presented by J. T. Lofton)

Scientists at the Southern Regional Research Laboratory and other laboratories have shown that treating cotton fabrics with durable polymers extends the wear life and improves the smooth-drying appearance of all-cotton durable-press fabrics. Research on polymer-treated fabrics has been reported by Abrams and Sherwood (1); Blanchard, Harper, Gautreaux, and Reid (4); Harper, Blanchard, and Reid (5); Sherwood (6); and Wolfgang (7). Researchers at the Southern Retional Research Laboratory are still exploring the use of polymers in finishes for woven cotton fabrics to upgrade certain properties for specific end uses.

This paper is a progress report of research conducted to develop improved all-cotton fabrics for use in durable-press garments through the application of polymers to cotton yarns before weaving and to determine the effects of fabric structure and finishing processes on the physical properties and wearability of these fabrics. Experiments in the initial phase were designed to find the two best performing polymers to be used for the subsequent phases of this project. The basis for the selection of these two polymers were: (1) Their contribution to the desirable properties needed in cotton durable-press fabrics, and (2) their effectiveness as a size in the weaving process.

Exploratory work showed that fabrics woven from polymer-sized yarns and treated with resins by postcure techniques had a desirable hand without the boardiness frequently associated with polymer-treated fabrics. Cuffs fabricated from these experimental fabrics sustained 50 home-type launderings without damage and retained a warp plus filling wrinkle recovery angle of 300°.

MATERIALS AND METHODS

The polyurethane latices used in this investigation were listed as E-406 and E-503 produced by Wyandotte Chemical Corporation.

The polyacrylates used were E-269 and E-358 produced by Rohm and Haas.

The other polymer used was a commercial butadiene styrene copolymer with a trade name of Pliolite Number 2498 produced by Goodyear Tire and Rubber Co.

Crosslinking agent Permafresh 183 and 183K, along with Catalyst X-4 (Sun Chemical Co.), and softeners used in this work were commercial products. Permafresh 183K is a low temperature curing resin. Another crosslinking agent used, dimethylol methoxyethyl carbamate (DMMXEC), was UCET Carbamate Finish 4G marketed by Union Carbide. The polyvinyl alcohol was DuPont's Elvanol 50-42 and the carboxymethylcellulose was Hercules' CMC Warp Size.

Yarns used in this work were spun from a two-bale blend of Acala 4-42 cotton processed in a conventional manner. All fabrics were woven from one warp count, 40 tex (15/1 cotton count), and one filling count, 50 tex (12/1 cotton count). In all cases the woven fabrics were 74 x 54 thread count, 2/2 regular twills weighing approximately 7 oz./sq.yd. Warp yarns and some filling yarns were sized on a laboratory continuous range which was modified to operate as a hot air slasher. Filling yarns were also sized in skein form.

Test procedures—To determine the physical properties of the treated fabrics, 1-yard samples of each were pressed in a steam-heated automatic press on cotton setting and cured for 8 minutes in a circulating oven set for 320° F. The cured samples were washed to remove unreacted resin and catalyst and then tumble-dried. After the samples were dried, ASTM test procedures (3) were followed in determining their physical properties.

To determine performance in the washing machine, four 12-inch long by 9-½-inch wide cuffed trouser legs were made from each of the experimental fabrics. These were pressed, cured, and then subjected to repeated laundering. The cuffs were laundered in 4-pound batches in a Kenmore Model 600 washing machine.

The washed cuffs were tumble dried for 45 minutes in an electrically heated Kenmore Model 600 drier at a temperature of about 140° F. The cuffs were examined after each five cycles of laundering. Any rupture at one location was classified as a hole and recorded. Cuffs were graded for wash-wear and crease ratings after the first and thirtieth laundry cycles. The wash-wear ratings were determined by use of overhead lighting with the AATCC Three Dimensional plastic replicas while crease ratings were determined with AATCC Photographic Standards (2).

RESULTS AND DISCUSSION

Durable-press fabrics woven from polymer-sized yarns were compared with control fabrics treated in a conventional manner and with control fabrics with combination treatments equivalent to the finishes given the yarn-treated fabrics.

Fabrics woven from polymer-treated warp and filling yarns—Thirty-two experimental fabrics were woven from warp and filling yarns treated with four different polymers. These thirty-two fabrics consisted of two replicates of the 16 possible combinations of the four polymer-treated yarns using a polymer-treated yarn in both the warp and filling direction. The design and identification of the experiment are shown in table 1.

The same concentration of a given

Table 1.—Design and identification of polymer-treated yarn experiment

Filling	Warp Polyacrylate 358 A	 Butadiene styrene copolymer B	 Poly-urethane E-406 C	 Poly-acrylate 269 D
Polyacrylate 358-A	AA	BA	CA	DA
Butadiene-styrene copolymer-B	AB	BB	CB	DB
Polyurethane 406-C	AC	BC	CC	DC
Polyacrylate 269-D	AD	BD	CD	DD

polymer was used for both the warp and filling yarn treatments. The warp yarns were slashed under tension while the filling yarns were treated in skeins, dried, and rewound for quilling. The fabrics woven from these treated yarns were scoured and bleached without appreciable stripping of the polymer. Each yarn-treated fabric was given a pad-dry-cure treatment with 5 percent solids solution of Permafresh 183.

Control fabrics were woven from starch-sized warp yarns and untreated filling yarns. The control fabrics were desized, scoured, and bleached. Parts of the control fabrics were given a conventional pad-dry-cure treatment using a padding solution containing 6 percent solids of Permafresh 183. Additional lengths of the control fabric were treated with each of the four polymers and dried. The polyurethane and the butadiene-styrene copolymer pad bath contained 16-percent polymer solids while the polyacrylate pad-bath contained 12-percent solids. The polymer-treated control fabrics were given a pad-dry-cure treatment using a padding solution containing 5-percent solids of Permafresh 183.

Table 2 shows the strength properties of two fabrics woven from warp and filling yarns pretreated with Polyacrylate E-358 and Polyurethane E-406. These fabrics were compared with the control fabrics which were given the same polymer treatments in fabric form. The results show that the polymer-treated fabrics have substantial improvement over the standard crosslinked fabrics in both breaking and tearing strength. Generally, the yarn-treated samples show a modest improvement over the fabric-treated samples in strength properties. The polyacrylate samples had slightly better strength properties than the polyurethane samples. Breaking strength retention in

Table 2.--Strength properties of fabrics

Property	Untreated	X-linked control	Yarn-treated Poly-acrylate	Yarn-treated Poly-urethane	Fabric-treated Poly-acrylate	Fabric-treated Poly-urethane
Breaking strength						
Warp, pounds	91.8	46.1	73	67.8	67.7	71.1
Filling, pounds	89.8	33.5	51	43.6	45.1	47.4
Tearing strength:						
Warp, grams	4,666	1,533	2,567	2,233	R[1]	2,367
Filling, grams	4,666	1,267	2,533	1,867	1,733	2,000

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[1] Tear reverted to crosswire direction of specimen.

Table 3.--Abrasion properties and wrinkle recovery angle of fabrics

Property	Untreated control	Control X-linked	Yarn-treated Poly-acrylate	Yarn-treated Poly-urethane	Fabric-treated Poly-acrylate	Fabric-treated Poly-urethane
Flex abrasion (cycles):						
Warp	1,718	52	846	803	599	452
Filling	1,488	42	414	502	318	398
Flat abrasion (cycles)	481	261	480	565	456	524
Conditioned wrinkle recovery angle (WRA) (W+F)	201	308	281	295	309	322

Table 4.—Laundry performance of cuffs with yarn and fabric polymer treatments

		Yarn-treated		Fabric-treated	
Property	Control X-linked	Poly-acrylate E-358	Poly-urethane E-406	Poly-acrylate E-358	Poly-urethane E-406
Wash-wear rating:					
After 1st wash	4.7	4.2	4.7	4.6	4.6
After 30th wash	4.7	4.3	4.4	4.5	4.4
Crease sharpness:					
After 1st wash	5.0	4.3	4.8	4.9	4.8
After 30th wash	4.7	4.3	5.0	5.0	5.0
Average laundry cycles to failure	5	46	27	27	16

the polymer-treated samples was much better in the warp direction than in the filling direction. Warp breaking strength retention after crosslinking for the 16 yarn-treated fabrics ranged from 69 to 104 percent relative to the untreated control. Filling strength retention ranged from 48 to 63 percent relative to the untreated control. Although breaking strength retention is usually greater for the warp yarns than for the filling yarns, an even greater difference occurred in this case. The comparative figures for the conventionally finished control were 38- to 51-percent retention in the warp and 32- to 37-percent retention in the filling. The high warp breaking strength retention of fabric woven from the polymer-treated yarns may be caused by the better coverage and polymer orientation achieved in warp sizing under tension. This is not so when the filling yarns are treated in a relaxed state such as skein form.

In table 3, the abrasion properties of polymer-treated fabrics and control-treated fabrics are shown. These data show that polymer-treated fabrics have much better performance than the conventionally crosslinked controls. While the fabrics woven from polymer-treated yarns had somewhat better abrasion resistance than the fabric-treated samples, they also possessed moderately reduced wrinkle recovery angles.

In table 4, wash-wear, crease sharpness and cuff laundry abrasion data for these treatments are presented. The cuffs prepared from the yarn-treated fabric had

Table 5.–Strength properties of fabrics[1] with low resin treatments

Property	Fabrics					
	Polyacrylate E-358(yarn) Permafresh 183(fabric)			Polyurethane E-406(yarn) Permafresh 183(fabric)		
	10 pct.	12 pct.	14 pct.	10 pct.	12 pct.	14 pct.
Breaking strength:						
Warp, lb.	83	73	64	84	86	74
Filling, lb.	66	54	45	64	61	56
Tear strength:						
Warp, lb.	7.2	4.8	4.8	8.1	5.8	5.8
Filling, lb.	5.5	4.0	4.0	5.6	4.8	4.5

[1] Fabrics treated with Permafresh 183.

properties superior to both the conventional controls and the polymer fabric treated controls. The cuffs fabricated from the polyacrylate-yarn-treated fabric went 46 laundry cycles before damage, while the cuffs fabricated from the polyacrylate-treated fabric went 27 laundry cycles. Part of this improvement might be because of the lower wash-wear appearance of the cuffs made from the yarn-treated fabric. With the polyurethane-treated cuffs, the improved performanee of the yarn-treated cuffs could not be ascribed to this reason since both types of cuffs had equivalent appearance ratings. The polyurethane-yarn-treated cuffs went 27 laundry cycles before damage as compared with 16 laundry cycles for the fabric-treated samples. In this series the conventionally finished control went five cycles before damage occurred.

The fabrics treated with polymers at the yarn stage generally had a softer hand than fabrics treated with polymers in the fabric stage. Tinius-Olsen[1] stiffness values were approximately the same with one polyacrylate and a polyurethane. The other polymers showed decided differences. The fabric treated with butadiene-styrene copolymer had a bending moment of 11.5×10^{-4} and 7.25×10^{-4} in. lb. in the warp and filling, respectively, compared to values of 8.0×10^{-4} and 5.25×10^{-4} in. lb. for the equivalent yarn-treated fabric. Similarly, the fabric treated with the

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[1] Federal Specifications CC-T-191b, Test 5205.

Table 6.—Yarn-treated fabrics with low resin treatments

Property	Fabric					
	Polyacrylate E-358 Permafresh 183			Polyurethane E-406 Permafresh 183		
	10 pct.	12 pct.	14 pct.	10 pct.	12 pct.	14 pct.
Conditioned wrinkle recovery angle (WRA) (W+F)	232	280	269	266	298	287
Avg. laundry cycle to failure	35+	30	25	35+	25	23
Wash-wear rating						
1st wash	3.3	3.9	4.0	4.2	4.2	4.7
30th wash	3.7	4.5	4.5	3.7	4.7	4.9

second polyacrylate had warp and filling stiffness values of 15.5 $X10^{-4}$, and 12.0 $X10^{-4}$ in. lb., compared to values of 7.0 $X10^{-4}$ and 7.5 $X10^{-4}$ in. lb. for the yarn-treated fabrics.

Since lower concentrations of resin appear to be effective with polymer yarn-treated fabrics, lower concentrations of Permafresh 183 were used to determine the resin level necessary to give wash-wear and crease ratings of four or better after 30 laundry cycles. The fabrics were treated to obtain resin add-ons of 3, 3.5, and 4 percent solids using baths containing 10, 12, and 14 percent solutions of Permafresh 183.

Some of the physical properties of the treated fabrics are given in table 5. The appearance and laundry performance of these fabrics in test cuffs are given in table 6. It is noticeable that strength properties decrease with progressively higher resin add-ons. This suggests that no higher resin treatment should be used on these fabrics than is necessary to achieve the desired level of appearance and dimensional stability. The results indicate that adequate performance can be achieved with a resin bath containing 5.4 to 6.3 percent solids of Permafresh 183.

Fabrics with different polymers on warp and filling—A number of fabrics with one polymer on the warp and a second polymer on the filling was also investigated. While each of these fabrics had different properties after crosslinking, for the most part, the properties were not unlike the properties of the fabrics woven from warp and filling yarns treated with

Table 8.—Properties of fabric sized with polyurethane and polyvinyl alcohol

Property	Fabric			
	Warp treated only		Warp and filling treated	
	Grey X-linked	Scoured X-linked	Grey X-linked	Scoured X-linked
Breaking strength:				
Warp, lb.	62	53	88	61
Filling, lb.	40	29	77	50
Tearing strength:				
Warp, lb.	5.5	4.4	6.0	3.9
Filling, lb.	3.1	2.3	5.4	3.2
Conditioned wrinkle recovery angle (WRA) (W+F)	318	301	296	320
Average laundry cycle to failure	10	10	12	5
Tinius-Olsen stiffness:				
Warp, $X10^{-4}$ in. lb.	20.2	12.5	27.0	13.5
Fill, $X10^{-4}$ in. lb.	7.0	5.5	19.5	8.0

cuffs treated by this method was approximately twice that of the control fabric cuffs. The failure to achieve better abrasion performance is probably because of the stiffness of the fabrics. Warp and filling stiffness values were 27 $X10^{-4}$ and 19.5 $X10^{-4}$ in. lb., respectively, compared to the usual values of approximately 10-12 $X10^{-4}$ in. lb. for the controls without polyvinyl alcohol.

The fabric woven from yarns sized with polyurethane and resized with polyvinyl alcohol showed slightly better abrasion properties but lower strength properties than the fabrics woven from yarns sized with a one-bath mixture of polyurethane and polyvinyl alcohol.

Further experiments were conducted in which a mixture of polyvinyl alcohol and polyurethane was used in sizing; the fabrics were given lower level crosslinking treatments using 12-percent Permafresh 183 and 6-percent dimethylol methoxyethyl carbamate. Some of the fabric properties and the laundry performance of the cuffs are listed in table 9. A combina-

Table 9.—Tear strength and laundry performance of fabrics

Property	Fabric: Warp treated only, 12 pct. Perma-fresh 183	Fabric: Warp treated only, 6 pct. DMMXEC	Fabric: Warp and filling treated, 12 pct. Perma-fresh 183	Fabric: Control, 20 pct. Perma-fresh 183
Tear strength:				
Warp, lb.	5.0	7.05	6.4	3.4
Filling, lb.	3.4	4.8	4.15	3.0
Conditioned wrinkle recovery angle (WRA) (W+F)	304	295	289	293
Average laundry cycle to failure	20	25	35	7.7
Wash-wear rating:				
35th Wash	5.0	5.0	5.0	4.7

tion of high wash-wear performance and superior abrasion resistance at a low level of resin add-on has been achieved with this system.

Dye treatments—To assess the dyeability of fabrics with polymer-treated yarns, commercial denim warp yarns were sized with three different formulations: (1) Conventional starch size; (2) 16-percent emulsion of polyurethane; and (3) one-bath mixture of 8-percent polyurethane and 2 percent CMC. A 10 oz./yd.^{2} denim fabric was woven from each warp using an untreated filling. Portions of these fabrics were desized, scoured, and bleached. The fabrics were sewn together and dyed with Indanthrene Blue BPWF 70-percent and Ponsol Olive GGLD 14-percent on weight of fabric. All three fabrics dyed level. The control was slightly darker in shade than the two fabrics with polyurethane-treated warps. There was no apparent difference in color shade of the yarn-treated fabrics even though one had twice the polyurethane of the other. Samples were treated with Permafresh 183 and made into cuffs, pressed, cured, and subjected to repeated laundering for evaluation of differences in fading and frosting. When cured, the polymer treated and control fabrics showed a distinct shade difference. The color change was attributed to the discoloration of the polyurethane. However, the preliminary results suggest that with

Table 10.–Comparison of wrinkle recovery and crease sharpness

Treatment 1/	Conditioned wrinkle recovery angle				Crease sharpness 30th wash
	1st wash		30th wash		
	Warp	Filling	Warp	Filling	
					Degree
Conventional	141	139	114	104	62
Fabric polymer treated	160	160	150	148	32
Warp and filling yarns polymer treated	159	162	152	151	27
Warp yarns polymer treated	156	139	152	123	58

1/ All fabrics were padded with 16-percent Permafresh 183, 1-percent polyethylene and crosslinked.

a proper combination of dye, dye technique and polymer size, the fabrics would be dyeable in fabric form.

Special effects with yarn-treated fabrics–The polymer yarn-treated fabrics require less crosslinking agent to achieve durable-press performance. This permits the accomplishment of certain special effects if proper selection of fabrics is made. As an example, two-ply yarns were sized with 16-percent polyurethane and woven into a 7 oz./sq.yd. tight-weave fabric with polyurethane-treated yarn in both the warp and filling. Three-percent polyethylene was applied to the fabric. The fabric was fabricated into a cuff, pressed, and cured for 10 minutes at 150° C. This cuff had a wash-wear rating of 4.0 and a sharp, acceptable crease after 30 launderings. The wrinkle recovery angle of the fabric was 275° after the first wash. A precure finish using 4.5-percent DMDHEU was applied to another sample of this fabric. The sample was cured, washed, and made into a cuff that was pressed and heat set at 150° C. This cuff had a conditioned wrinkle recovery angle (W+F) of 303°, a wash-wear appearance of 4.5, and a reasonably sharp crease after 30 launderings. The technique seems to work with loosely woven or lightweight fabrics.

An improvement in wrinkle recovery or crease sharpness can be controlled to apply only to one direction of the yarns in the fabric system. For example, table 10 shows that the wrinkle recovery performance of the fabric treated with polyurethane has a similar performance to the fabric woven from warp and filling yarns treated with polyurethane. When the polymer is applied only to the warp yarns, the warp WRA is equivalent to the WRA of the polymer-treated fabric while the filling wrinkle recovery is quite similar to the filling wrinkle recovery value of the conventionally finished fabric without polyurethane.

Analogous performance can be noted in crease sharpness values. The polyurethane-treated yarn fabric and the polymer-treated fabric listed in table 10 have low crease sharpness values of 27° and 32°, respectively. In contrast, fabrics with only the warp yarn polymer–treated have a crease sharpness value of 58°. This value is similar to the conventional finish value of 62°. The method of applying polymer only in the warp gives the advantage of increased wrinkle recovery and abrasion resistance in the warp direction without the increased crease sharpness which occurs when both the yarn systems are polymer-treated or when the fabric is polymer-treated.

SUMMARY

A permanent warp size can be utilized as an integral step in fabric weaving and finishing. Fabrics woven from polymer-treated yarns require a slightly lower level of crosslinking agent than fabrics treated with polymers. Similarly, fabrics woven from polymer-treated yarns usually have slightly better physical properties after crosslinking and offer moderate improvement over polymer-treated fabrics in abrasion performance. In contrast to the fabric-treated samples, application of polymers before weaving frequently lead to softer fabrics at the same level of polymer load.

The weaving of a warp yarn treated with one polymer in combination with an untreated filling or a filling treated with a different polymer leads to unique fabrics that cannot be duplicated by treatment of fabric with polymers. By proper selection of the polymers, a certain amount of tailoring of fabric properties can be accomplished.

In addition to a 100 percent permanent polymer size, several fabrics have been reported on in which a mixture of permanent and temporary sizing agents were used. Starch, CMC, and polyvinyl alcohol have been used as temporary sizing agents in combination with permanent polymers such as polyurethane. This permits the use of a lower level of permanent polymer add-on with good weavability of the warp yarns.

Residual polyvinyl alcohol can be further utilized to improve strength retention in conjunction with a polymer treatment. In one such case, a fabric was produced with 95-percent retention in warp breaking strength and 85-percent retention in filling breaking strength with a WRA of 296°. Despite these strength retention properties, control of fabric stiffness must be achieved before superior abrasion performance is obtained.

Another type of fabric can be produced by use of permanent polymer sizing in the warp only. Such a fabric has increased polymer protection and wrinkle recovery in the warp direction without the increased crease sharpness that occurs when both the warp and fill yarns are treated and when the fabric is polymer treated.

Certain special effects can be produced with the yarn-treated fabrics. It has been possible to produce 2-ply 7-ounce tightly woven fabric with good wash-wear appearance and crease sharpness with only a polymer finish. Furthermore, a low level crosslinking treatment has been utilized to produce a durable-press cuff with acceptable crease performance after 30 launderings. Such a fabric may alleviate the formaldehyde release and alteration problem usually associated with postcure goods.

Finally, initial experiments indicate that fabrics woven from polymer sized yarns can be dyed in the fabric state.

Research on the use of polymer sizes to improve the performance of durable-press cotton fabrics is continuing; however, a preliminary report of the current findings was deemed to be desirable at this time.

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REFERENCES

1. Abrams, E., and Sherwood, N. H. 1953. Nitrile Rubber Latices as Permanent Abrasion-Resistant Finishes for Blue Denim Fabric. Amer. Dyestuff Rptr. 42: 777-782.

2. American Association of Textile Chemists and Colorists. 1965. AATCC Tentative Methods 88A-1964T and 88C-1964T. Tech. Manual 41: B99-103, B104-105.

3. American Society for Testing and Materials. 1966. ASTM D1295-53T, D1682-59T, D1424-59, D1175-55T.

4. Blanchard, E. J., Harper, R. J., Jr., Gautreaux, G. A., and Reid, J. D. 1967. Urethanes Improve All-Cotton DP. Textile Indus. 131(1): 116-119, 122, 143.

5. Harper, R. J., Blanchard, E. J., and Reid, J. D. 1967. Acrylates Improve All-Cotton DP. Textile Indus. 131(5): 172, 174, 177, 181, 184, 186, 233, 234.

6. Sherwood, N. H. Nitrile Latices A New Concept in Textile Finishing. 1955. Amer. Dyestuff Rptr. 44: P262-P264.

7. Wolfgang, W. G. 1966. Heading to Market: Polyurethane Resins that Boost Abrasion Resistance. Textile World 116(1): 104-106, 108, 110.

DISCUSSION

Question: I know that the research was done on dyed fabrics, but I would like to know if any trouble was experienced with dye fastness, light fastness, and crocking, where the dye was on top of the urethane.

Mr. Lofton: Information in this area is not available at present; however, tests are still in progress.

Question: The figures on the slides are good and I would like to know if Mr. Lofton had any rough estimates as to the cost of a fabric made by the polymer sizing technique.

Mr. Lofton: The economics of the process are not known because the research has not progressed far enough to establish the amount and type of polymers needed for sizing.

Question: What class of dyes are used on the fabrics?

Mr. Lofton: A regular vat dye was used.

Question: Were the yarns treated with polymer prepared for dyeing before the fabric was desized, scoured, and bleached?

Mr. Lofton: The yarns were not desized or scoured before weaving; only the woven fabric was desized and scoured.

ELECTROSTATICS, OZONE, AND COTTON

by
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(Presented by A. Baril, Jr.)

INTRODUCTION

Research effort of the Machine Development Section in the Cotton Mechanical Laboratory at the Southern Utilization Research and Development Division is being channeled toward the development of a completely new system for the processing of cotton fiber into yarn. It has been proposed that such a system could utilize relatively new principles in the areas of aerodynamics, ultrasonics, and electrostatic forces to replace those now employed and do the job better, faster, and more economically.

Modest beginnings have been made in basic research programs to obtain fundamental information in each of these fields. The furthest advanced of these studies is in the area of electrostatics. It has been reported 1/ that cotton fibers can be separated, fractionated, aligned, and manipulated by an electric field. Although progress has been made, electrostatic devices for handling fibers are still in the experimental stage of development. Additional basic information is being accumulated and evaluated to answer many of the obvious questions that arise when cotton fibers are subjected to unique force fields.

1/ Kassenbeck, P. Method of and Apparatus for Processing Textile Fiber Material. U. S. Patent No. 2,977,475. 1961.

Lafranca, J. J., Mayer, M., and Weller, H. W. Electrostatic Separation of Fibers, Will It Replace Mechanical Combing? Textile World 116(6): 58-61. 1966.

______________, Mayer, M., and Weller, H. W. Fiber Fractionating Apparatus and Process. U. S. Patent No. 3,346,110. 1967.

Mayer, M., Weller, H. W., and Lafranca, J. J. Electrostatic Fiber Fractionation. Textile Bull. 91 (3): 50, 52-54. 1965.

______________, Weller, H. W., and Lafranca, J. J. Fiber Fractionating Apparatus and Process. U. S. Patent No. 3,341,007. 1967.

Oglesby, S., Jr., and Thomas, A. L., Jr. Method and Apparatus for Collecting Fibrous Material and Forming It Into a Strand. U. S. Patent No. 2,711,626. 1955.

It is known that in electric fields ozone will be produced between the electrode in free air even when the discharge is silent. Since ozone occurs, what happens to the cotton fiber when subjected to an electric field? Are any of the fiber's physical or chemical properties degraded, altered, or enhanced?

To answer these questions, an experiment was designed for subjecting samples of cotton fibers to an ozone generating electric field and to ozone alone. By comparing these treated samples with untreated control samples, it was determined whether fiber property changes had occurred and whether they were attributable to the ozone, the electric field, or a combination of both.

PROCEDURE

Acala 4-42 variety cotton, grown under irrigated conditions, was used throughout the tests. The cotton was 1-1/32 inch staple, 4.61 Micronaire, and 78-percent maturity. In preparing the fibers, 100-gram samples were opened by one pass through the SRRL Non-Lint Tester before placement in either of the irradiation areas.

The samples of cotton fibers were irradiated by an air-ozone mixture in a 6-inch diameter 5-foot long pyrex tube with an airtight seal at each end, fig. 1. Each sample was placed in a wire frame and at a fixed position within the tube to assure the same volume occupancy and location for all samples. The tube was sealed and connected to the output of a Welsbach Model T-23 Ozonator.

The Ozonator delivered a given concentration of ozone at a predetermined flow rate. In this evaluation three levels of ozone were selected: 7 mg./1., 14mg./1., and 21 mg./1. at a delivery rate of 0.04 Std. CFM using an air supply pressure of 7 p.s.i. to the ozonator. The ozone generator was calibrated by using the potassium iodide method since an ozone level meter demonstrated too much drift.

The experimental procedure consisted of calibrating the generator for a given ozone concentration, inserting a sample of cotton, irradiating the sample, purging the system, and recalibrating. The system was monitored to assure that a constant supply of ozone was being supplied.

At each level of ozone, samples were irradiated for three time intervals—5, 10, and 15 minutes—with a replication of three, giving a total population of 27 samples evaluated.

For the electrostatic evaluation, a free electric field was maintained between two 24-inch square aluminum plates with an air gap of 2 inches (fig. 2). The potential difference was supplied by a regulated direct current power supply having a maximum output of 60 kilovolts at 1 milliampere.

Each sample opened by the SRRL Non-Lint Tester as in previous tests was placed over the area of the plates to give a 1-inch layer of cotton fiber. When the field was excited this mass of cotton expanded quickly and uniformly to fill the

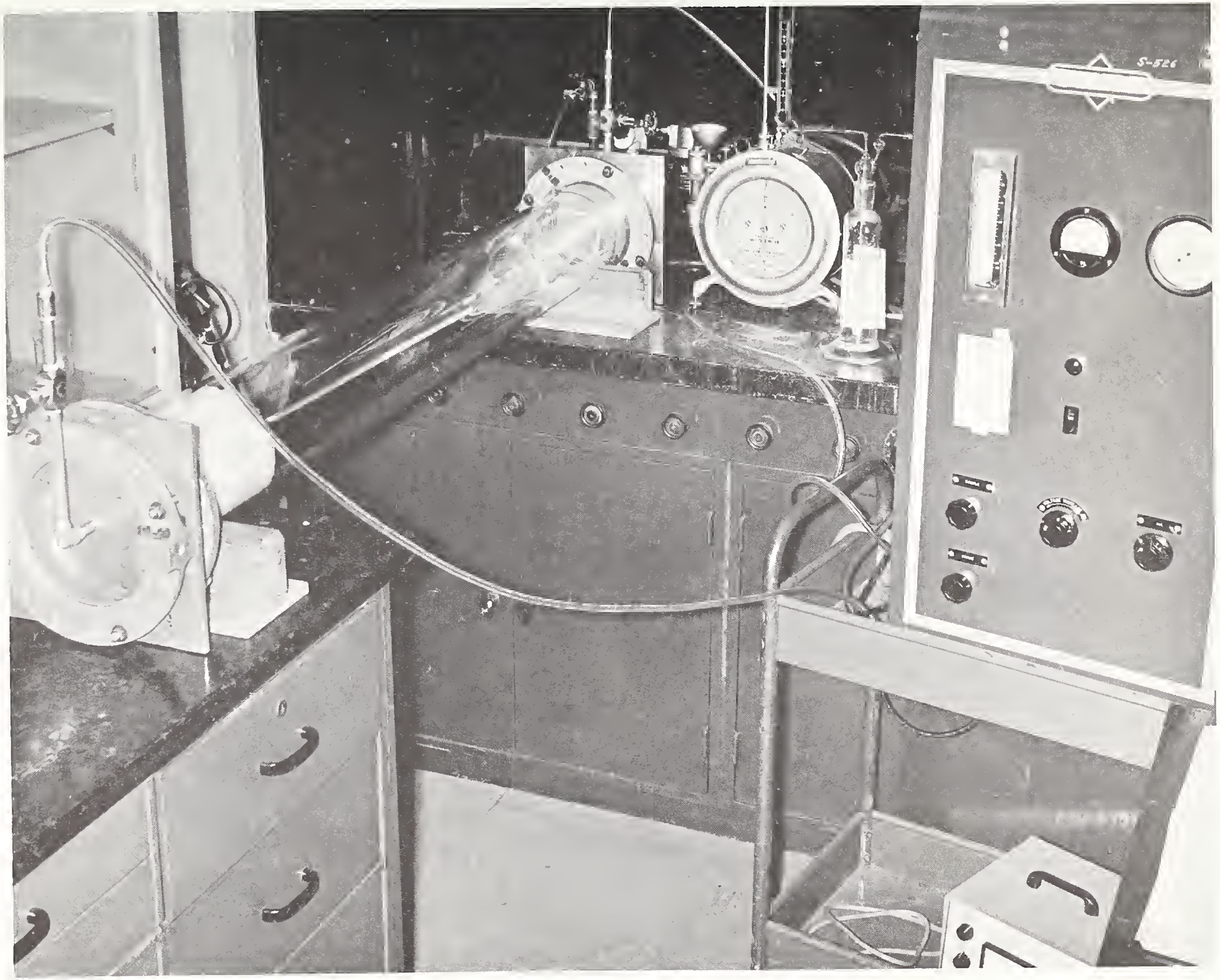

Figure 1.–Ozone exposure apparatus.

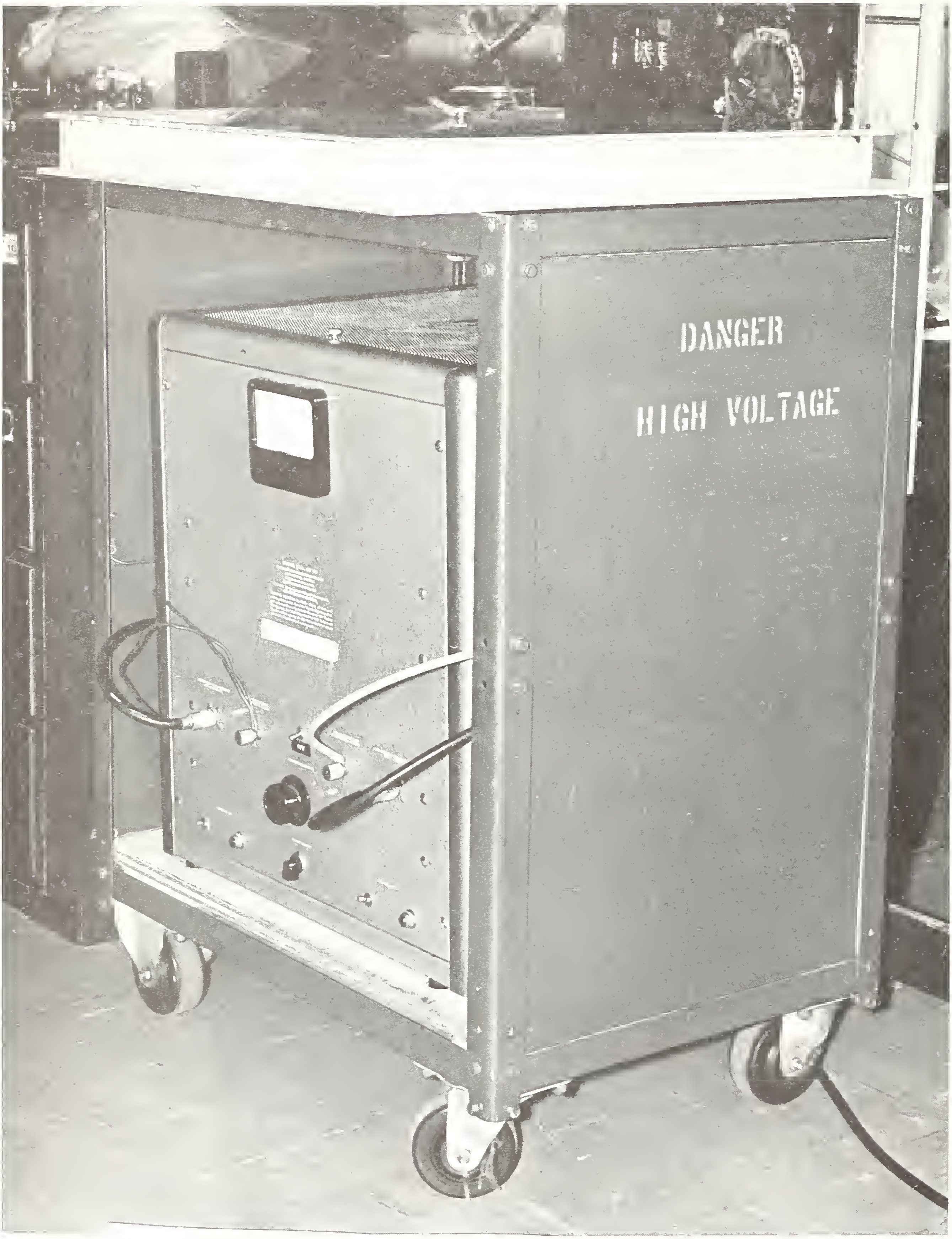

Figure 2.–Electrostatic exposure apparatus.

2-inch air gap. Exposure was made at three potential gradients, 10, 15, and 20 kilovolts per inch. At each level three time periods 2, 5, and 10 minutes, were used and a replication level of three was maintained throughout the experiment. The system was monitored to assure that ozone was produced during exposure. This was accomplished by placing a sample of potassium iodide treated cotton in the electric field and noting the color change.

The following tests were used to assess changes in the cotton fibers that might have occurred as a result of exposure to ozone or the electric field.

RESULTS

To facilitate presentation of the data, all of the experimental results are not discussed in this paper. The maximum and minimum levels of treatment for both the ozone and electrostatic exposures were selected as representatives.

In table 1, the Micronaire readings and the fiber length determinations for the control, ozone treated, and electrostatically exposed samples show little or no variation is observed values for all treatment conditions. The values for tenacity and bundle elongation show no

Micronaire:	Determination of fiber fineness, ASTM Designated D 1448-59
Fiber length:	Determination of cotton fiber length, ASTM Designated D 1440-55
Strength and elongation:	Cotton fibers, flat bundle method (Stelometer), ASTM Designation D 1445-64T
Moisture determination:	Moisture content and moisture regain of cotton (oven method). ASTM Designation D 2495-61T
Alkali-centrifuge value:	Determination according to procedure of Marsh, P. B., Merola, G. V., and Simpson, M. E. Textile Research Journal 23(11): 831 (1953) as modified by Honold, E., and Grant, J. Textile Industries, in press (1968).
Differential dye test:	According to procedure of Goldthwait, C. F., Smith, H. O., and Barnett, M. P. Textile World 97(7): 105 (1947).
Friction shear:	According to procedure of Hertel, K. L. Textile Bull. 93(4) (1967).
Individual fiber:	According to procedure of McBride, T. E. M. S. Thesis, August 1965, Georgia Institute of Technology.

significant change under either form of treatment.

The calculated values, toughness and stiffness, show slight differences, but these are not statistically significant. Moisture regain was not affected by exposure to either the ozone or the electric field.

Samples of both ozone and electric treated cotton were evaluated for individual fiber friction and shear friction. Because of the difficulty encountered in obtaining meaningful data for individual fiber friction, very limited data were collected. Measurements were made on four fiber pairs of each type treatment, control, ozone, and electrostatic. Three successive measurements were made for each fiber pair. The average values for the 36 measurements are given in table 2. The data are remarkable because of their consistency. Although the data are limited and any one single series of measurement shows considerable variation, it was concluded that there was no marked difference in individual fiber friction properties for the three types of exposed fibers; perhaps the slight decrease in static friction of the ozone and electrostatic treated fibers may be real.

In addition to the single fiber friction study, a very limited evaluation of shear friction was made on all three samples of cotton, control, ozone, and electrostatic. It was concluded that the treated cotton could not be distinguished from the control.

Table 1.–Fiber properties

Item	Control	Ozone exposed		Electrostatically exposed	
		7 mg/1 5 min.	21 mg/1 15 min.	10KV/in. 2 min.	20KV/in. 10 min.
Micronaire reading	4.61	4.63	4.68	4.68	4.74
Array mean length, in.	100	–	1.00	.99	1.00
Tenacity, g./tex	25.80	25.60	24.20	27.50	25.40
Bundle elongation, pct.	6.13	5.90	6.16	6.13	6.40
Toughness, g./tex	.79	.76	.75	.84	.82
Stiffness, g. tex	420.50	434.70	393.60	449.00	398.50
Moisture regain, pct.	6.33	6.28	6.45	6.35	6.35

Table 2.—Single fiber friction coefficient

Item	Kinetic	Static
Control	0.24	0.47
Electrostatic	0.235	0.46
Ozone	0.23	0.43

The test for swelling in alkali (table 3) indicated that the exposure to zone in high concentrations seems to cause some change in the cotton fiber. The magnitude of the change varies directly with ozone concentration and exposure time. The longer the exposure, the higher the alkali centrifuge values. Electric field irradiated samples show little or no change in the alkali centrifuge value regardless of potential gradient or length of exposure.

In anticipation that some difference in porosity could be detected, treated and control samples of cotton were tested by the Differential Dye Method. No observable differences were detectable.

To further evaluate the surface characteristics of the fibers, surface replicas were made of control, ozone, and electrostatically exposed fibers, and these were photographed through the electron microscope. Photographs shown in figure 3 are representative of the maximum conditions. Some cracks can be observed on the surface of the ozone irradiated fiber. The electrostatically irradiated fiber displays a preponderance of rugosities, however, small cracks can be observed on the surface of this fiber. It is of interest

Table 3.—Alkali centrifuge values. Control 192.63

Concentration	Ozone exposed		Electrostatically exposed		
	Exposure time		Potential gradient	Exposure time	
	5 min.	15 min.		2 min.	10 min.
7 mg./l	195.01	199.71	10 kv./in.	190.51	193.04
14 mg./l	201.30	214.24	15 kv./in.	192.34	193.48
21 mg./l	207.84	220.86	20 kv./in.	192.53	192.66

to note that the differences observed in the surface characteristics of the fibers obtained from the photomicrographic study and the alkali centrifuge values are not reflected by the test results for strength, fineness, and frictional properties of the fibers.

SUMMARY

The results of this study show that the cotton fiber properties are not being affected or altered significantly by the exposure to ozone or to the influence of ozone-generating electric field.

From this limited evaluation, the overall results encourage the application of electrostatics for manipulating cotton fibers in a radically new cotton textile processing system. Of the test results obtained, only the changes in the alkali centrifuge values and the cracks present on the fiber surfaces as seen on the electron microscope photomicrographs give any indication of possible change of fiber properties. What effect these changes of fiber surface characteristics have on sliver or yarn properties or in textile processing remains to be investigated.

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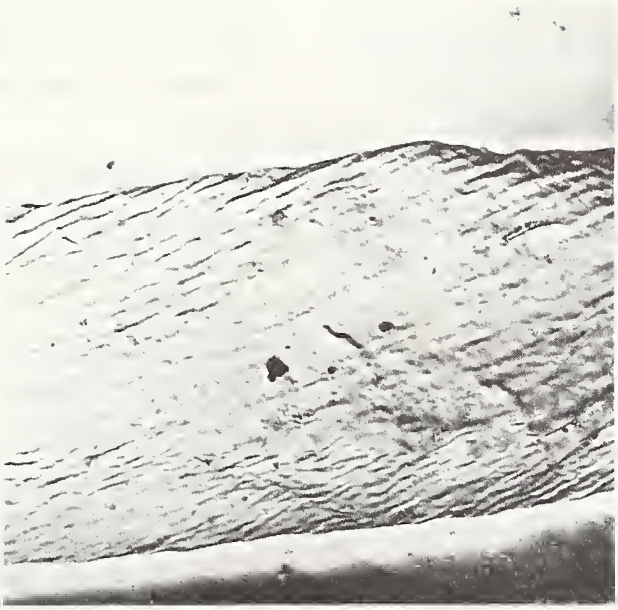
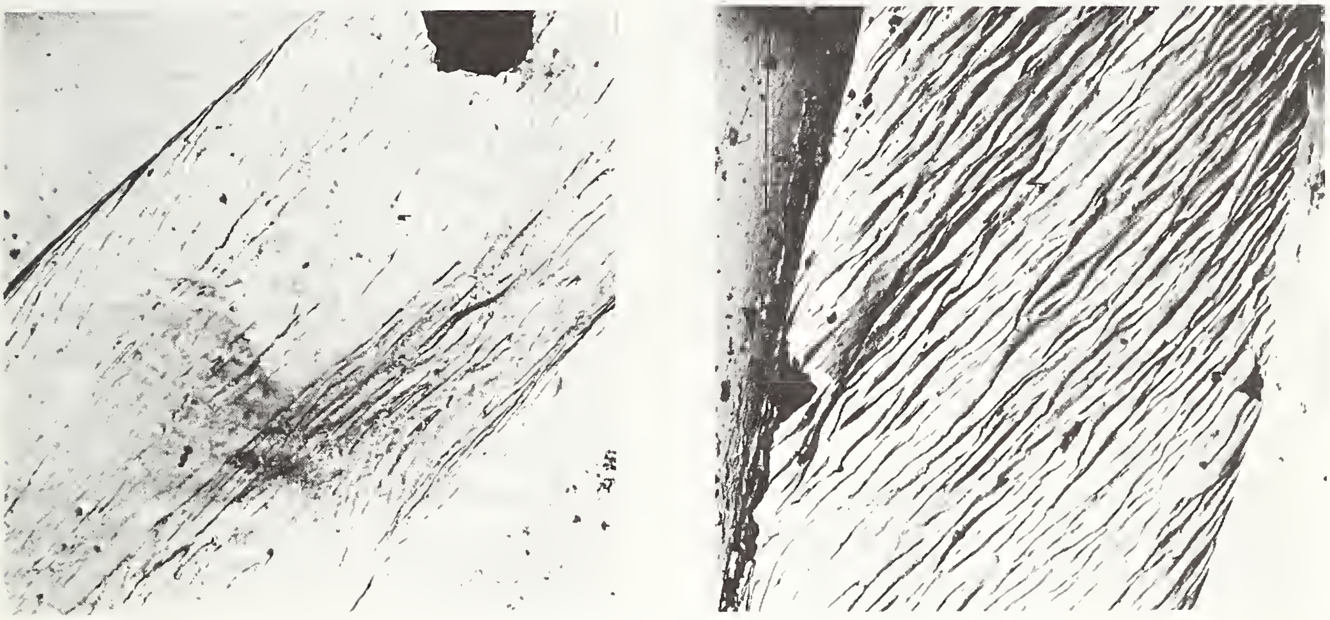


Control



Ozone Exposed

Electrostatically Exposed

Figure 3.—Electron micrographs of cotton fiber surface replicas.

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